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Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment

by

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Kurzbeschreibung

Zunächst wurde der Status des Biozidmonitorings in Deutschland und anderen EU-Staaten ausgewertet. Dazu wurden wissenschaftliche Veröffentlichungen und Berichte von Behörden und anderen Institutionen recherchiert. Um ein umfassenderes Bild zu erhalten, wurde ein erster internationaler Workshop zum Biozidmonitoring im Auftrag des Umweltbundesamtes und der NORMAN-Gemeinschaft organisiert. Hauptthemen waren Priorisierung von Bioziden für die Aufnahme in Monitoringprogramme, praktische Fragen der Probenahme und Analyse sowie die Auswertung von Monitoringdaten. Aufbauend auf einem Vorschlag aus einem früheren Projekt wurde ein Priorisierungsansatz für Biozide optimiert und umgesetzt. Die Stoffe werden im Hinblick auf mögliche direkte oder indirekte Emissionen, ihr Potenzial hinsichtlich nachteiliger Wirkungen, sowie ihre Relevanz für das Auftreten in Umweltkompartimenten (z.B. Wasserphase, Schwebstoffe, Biota) bewertet. Je nach Kompartiment werden stoffspezifische Eigenschaften wie die Verteilung zwischen den Medien, Persistenz sowie Bioakkumulation berücksichtigt. Um eine breitere Abdeckung von Bioziden im Umweltmonitoring zu erreichen, wurde ein Vorschlag für ein Biozid-Monitoringprogramm ausgearbeitet. In einem experimentellen Teil wurde ein Satz von Bioziden (Triclosan, Azolfungizide) sowie ein Transformationsprodukt (Methyltriclosan) in verschiedenen Proben aus Kläranlagen und Vorflutern untersucht. Die Belastungen mit den ausgewählten Stoffen waren an den untersuchten Standorten niedrig bzw. unter der Bestimmungsgrenze. In einer Studie zu Rodentiziden in archivierten Fischleberproben konnten geringe Konzentrationen von drei Verbindungen in Proben aus verschiedenen Jahren und Standorten nachgewiesen werden. Eine weitere experimentelle Studie zu Triclosan/Methyltriclosan belegt das Vorkommen von Rückständen beider Stoffe in Böden und Regenwürmern von klärschlammbehandelten Flächen. Schließlich wurden das vorgeschlagene Priorisierungsschema und das Überwachungskonzept auf Basis der experimentellen Ergebnisse und der Literaturauswertung diskutiert. Die Projektergebnisse wurden in einem zweiten Workshop zum Biozidmonitoring, der wiederum gemeinsam von Umweltbundesamt und NORMAN veranstaltet wurde, vorgestellt.

Abstract

First, the status of biocides monitoring in Germany and other EU countries was evaluated. Therefore scientific publications and reports by government agencies and other institutions were retrieved. To get a broader picture a first international workshop on biocides monitoring was organised on behalf of the German Environment Agency (UBA) and the NORMAN association. Main topics were prioritisation of biocides for inclusion in monitoring programmes, practical issues regarding sampling and analysis, and monitoring data evaluation. Based on a proposal from a previous project a prioritisation approach for biocides was optimised and executed. Compounds are evaluated for potential direct or indirect emissions, their potential to cause adverse effects, and their relevance for an occurrence in environmental compartments (e.g. water phase, suspended particulate matter, biota). Depending on the compartment, substance-specific properties relevant for partitioning between media, persistence and/or bioaccumulation are considered. To achieve a broader coverage of biocides in monitoring activities a proposal for a biocides monitoring programme was elaborated. In an experimental section a set of biocides (triclosan, azole fungicides) including one transformation product (methyltriclosan) was investigated in different samples from sewage treatment plants and receiving waters. At the investigated sites measured levels were low or even below the limit of quantification. In a study on rodenticides in archived fish liver samples low levels of three compounds could be detected in samples from different years and sites. An experimental study on triclosan/methyltriclosan proved the occurrence of residues of both compounds in soils and earthworms from sewage sludge treated sites. Finally, the proposed prioritisation scheme and monitoring concept was discussed on base of the experimental results and literature data. The project results were presented during a second international workshop on biocides monitoring again jointly organized by UBA and NORMAN.

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Abbreviations

AA	annual average
BPD	Biocidal Products Directive No. 98/8/EC
BPR	Biocidal Products Regulation No. (EU) 528/2012
dw	dry weight
EEA	European Environment Agency
ESB	Environmental Specimen Bank
EQS	environmental quality standard
LfU	Bayerisches Landesamt für Umwelt (Bavarian Environmental Agency)
LOQ	limit of quantification
PNEC	predicted no effect concentration
PPP	plant protection product
PT	product type
SPM	suspended particulate matter
STP	sewage treatment plant
TP	transformation product
UBA	Umweltbundesamt (German Environment Agency)
WFD	Water Framework Directive

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Zusammenfassung

Die EU Biozidprodukte-Verordnung (Nr. 528/2012) verursacht Veränderungen des Einsatzes von Bioziden und folglich ihrer Umweltkonzentrationen. Für Biozide, die in der Liste der genehmigten Stoffe aufgenommen wurden, könnten die Belastungen ansteigen, während für Stoffe, für die Nichtgenehmigungsentscheidungen getroffen oder Maßnahmen zur Risikobegrenzung implementiert wurden, verringerte Umweltbelastungen zu erwarten sind. Solche Konsequenzen können durch ein Umweltmonitoring nachgewiesen werden. Dabei könnte auch überprüft werden, ob die Umweltkonzentrationen oberhalb der abgeleiteten Wirkschwellen (z.B. sogenannte predicted no effect concentrations, PNECs) liegen. Doch bislang werden Biozide in den meisten Monitoringprogrammen nicht angemessen abgedeckt. Traditionell, z.B. in Gewässern, werden vor allem Pflanzenschutzmittel (teilweise auch als Biozide zugelassen), Stoffe, die aus industriellen Quellen stammen, und bestimmte ubiquitäre Schadstoffe überwacht. Ziel dieses Projekts war, einen Vorschlag für ein umfassendes Monitoringkonzept für Biozide zu erarbeiten. Damit soll zukünftig eine bessere Berücksichtigung von Bioziden in bestehenden Monitoringprogrammen erreicht werden.

Um einen Überblick über bestehende Biozidmonitoring-Aktivitäten in Deutschland und anderen europäischen Staaten zu erhalten, wurde im November 2012 vom Umweltbundesamt (UBA) und NORMAN, dem europäischen Netzwerk von Referenzlaboratorien und Forschungszentren für das Monitoring von Neuen Umweltschadstoffen (http://www.norman-network.net), gemeinsam ein erster internationaler Workshop zum Umweltmonitoring von Bioziden veranstaltet. Der Workshop diente als Plattform, um vorhandene Informationen und Daten zu Expositionspfaden von Bioziden auszutauschen, die Priorisierung von Bioziden für die zukünftige Aufnahme in Monitoringprogramme zu diskutieren, praktische Fragen der Probenahme und Analyse zu behandeln sowie die Datenverarbeitung und Auswertung von Monitoringdaten von Bioziden zu erörtern. Wichtige Themenkomplexe auf dem Gebiet des Biozidmonitorings wurden vorgestellt und in Arbeitsgruppen diskutiert.

Als Grundlage für die Umsetzung eines Biozidmonitoring in Deutschland wurde in diesem Projekt ein Konzept für die Priorisierung von Biozidwirkstoffen für ein kompartimentspezifisches Umweltmonitoring optimiert. Dazu wurde ein in einem Vorprojekt vorgelegter Vorschlag weiterentwickelt. Die in der Priorisierung berücksichtigten Biozide sind Verbindungen, für die (öffentlich oder vertraulich) EU Biozid-Bewertungsberichte als primäre Datenquellen zur Verfügung standen. Die Biozidwirkstoffe werden entweder derzeit im EU-Biozid-Altwirkstoffprogramm geprüft oder sind bereits nach der EU-Biozid-Produkte-Verordnung genehmigt. Häufig enthalten die Bewertungsberichte auch Angaben und Daten zu potenziellen Transformationsprodukten (TPs). Insgesamt wurden ca. 170 Verbindungen einschließlich der TPs in diesem Priorisierungsansatz berücksichtigt.

Das vorgeschlagene Priorisierungsschema besteht aus mehreren Schritten. In einem ersten Schritt werden die Stoffe hinsichtlich möglicher direkter oder indirekter Emissionen in Umweltmedien bewertet (vor allem basierend auf dem Verwendungszweck in bestimmten Biozid-Produktarten und deren Relevanz für Emissionen in Umweltmedien). Zusätzlich werden verfügbare Informationen zum Verbrauch, beispielsweise operationalisiert als Anzahl der in Deutschland registrierten Produkte mit dem entsprechenden Biozid, genutzt. Der zweite Schritt umfasst die Beurteilung möglicher schädlicher Auswirkungen der Biozidwirkstoffe auf Basis von Daten aus den Bewertungsberichten (z.B. PNECs). Im dritten Schritt wird die Relevanz der Biozidwirkstoffe für die Überwachung in verschiedenen Umweltkompartimenten beurteilt (z.B. Wasserphase, Schwebstoffe, Biota). Je nach Kompartiment werden in diesem Schritt auch relevante stoffspezifische Eigenschaften wie die Verteilung zwischen den Umweltmedien, die Persistenz bzw. das Bioakkumulationspotential betrachtet. Für jedes Kompartiment wurde schließlich eine Liste der als relevant priorisierten Biozide abgeleitet.

Um die Umsetzung eines umfassenden Biozidmonitorings vorzubereiten, wurden für relevante Umweltkompartimente Informationen zu existierenden Monitoringprogrammen in Deutschland zusam-

mengestellt. Soweit für verschiedene Kompartimente bislang keine Monitoringprogramme existieren, wurden Vorschläge für die mögliche Einführung erarbeitet, wobei u.a. Informationen zu Probenahme- und Analysenverfahren (einschließlich Qualitätssicherungsaspekten) aufgelistet werden. Informationen liegen nun für die folgenden Umweltkompartimente vor: Oberflächengewässer (Wasserphase, Schwebstoffe/Sediment, Biota), terrestrische Ökosysteme (Boden, Biota, Grundwasser), Kläranlagen (Abläufe, Klärschlamm), Atmosphäre. Für diese Kompartimente liegen auch Ergebnisse aus dem Priorisierungsansatz vor. Die erarbeiteten Informationen können den für das Monitoring zuständigen Institutionen zur Verfügung gestellt werden. Zur besseren Abdeckung von Bioziden im Oberflächengewässermonitoring wird die Zusammenarbeit mit den Bundesländern, die das Wasserrahmenrichtlinien-Monitoring umsetzen, empfohlen. Um auch eine retrospektive Verfolgung von Änderungen zu erlauben, wird die Nutzung von Proben aus Umweltprobenbanken vorgeschlagen. Archivierte Biota-Proben (z.B. Fisch- oder Greifvogelgewebe) können verwendet werden, um Trends unpolarer Biozide zu identifizieren. Polare Stoffe können in archivierten Schwebstoffproben aus Flüssen analysiert werden (Beispiele liegen vor). Spezielle Aspekte können in einem Schnappschussmonitoring untersucht werden (z.B. Antifouling-Wirkstoffe in Marinas). Für das Bodenmonitoring wird die Zusammenarbeit mit Bundesländern, die Bodendauerbeobachtungsflächen betreiben, empfohlen. Hier erscheinen Forschungsprojekte als am besten geeignet, beispielsweise zur Untersuchung von Bioziden auf Flächen, die mit Gülle oder Klärschlamm beaufschlagt wurden.

Bei der Bewertung der Monitoringdaten ist jeweils zu prüfen, ob die Wirkstoffe auch im Rahmen anderer Regelungen angewendet werden (z.B. als Pflanzenschutzmittel). In diesen Fällen ist es häufig nicht möglich, Umweltfunde einer spezifischen Nutzung zuzuordnen. Folglich konzentriert sich das Umweltmonitoring hier vorwiegend auf Stoffe, die nur als Biozide zugelassen sind. Alternativ können bestimmte Probenahmestrategien angewandt werden, um gezielt möglichst nur Biozideinträge zu erfassen (z.B. Untersuchung in bestimmten Jahreszeiten, wenn keine Anwendung als Pflanzenschutzmittel erfolgt oder in urbanen Regionen, wo eine Nutzung der entsprechenden Biozide als Pflanzenschutzmittelwirkstoffe nicht zu erwarten ist).

In einem experimentellen Projektteil wurden exemplarisch Untersuchungen zum Vorkommen relevanter Biozide in verschiedenen Umweltmedien durchgeführt. Ziel einer ersten experimentellen Studie war die Erarbeitung und Validierung einer einfachen Multiparameter-Methode für die Analyse einer Reihe von Bioziden in verschiedenen Umweltkompartimenten (Abwasser, Oberflächenwasser und Klärschlamm). Für die Analyse ausgewählter Proben wurden acht Zielanalyten festgelegt: Triclosan (antibakterieller Wirkstoff, für den aktuell die Nichtgenehmigung als Desinfektionsmittel verabschiedet wurde), Methyltriclosan (Transformationsprodukt von Triclosan), Cybutryn (Irgarol) und die Azolfungizide Propiconazol, Tebuconazol, Imazalil, Thiabendazol und Cyproconazol. Die Probenahmen erfolgten in sieben deutschen Kläranlagen und ihren korrespondierenden Vorflutern jeweils zu zwei Messzeitpunkten. Die Empfindlichkeit der Analytik wurde mittels Bestimmungsgrenzen (BG) charakterisiert und mit verfügbaren abgeschätzten Effektschwellen (PNECs) verglichen. Die untersuchten Proben zeigen sporadisch auftretende Belastungen mit den Zielanalyten. Fünf Azolfungizide und Methyltriclosan konnten in Abwasser und Oberflächenwasserproben detektiert werden. Ein Azolfungizid (Cyproconazol) wurde im Klärschlamm identifiziert. Belastungen mit den Zielanalyten sind in den Wasserproben dominanter als in den Klärschlammproben.

Die zweite praktische Untersuchung umfasste die Bestimmung von acht Rodentiziden (Antikoagulanzien) in Fisch. In Brassenleberproben von 17 Standorten in ganz Deutschland aus dem Archiv der Umweltprobenbank des Bundes (UPB) konnten Bromadiolon, Brodifacoum und Difethialon teilweise in Konzentrationen oberhalb der Bestimmungsgrenze nachgewiesen werden. Auf Basis der Ergebnisse aus dem räumlichen Vergleich wurden Proben von den Standorten Saar / Rehlingen und Elbe / Prossen für einen zeitlichen Vergleich ausgewählt. Von beiden Standorten wurden zehn Brassenleberproben aus dem UPB-Archiv retrospektiv analysiert (Zeitraum 1992-2013). Die Ergebnisse weisen keine eindeutigen Trends auf, aber Änderungen der Rodentizid-Konzentrationen von Jahr zu Jahr. Brodifacoum war der am häufigsten nachgewiesene Wirkstoff (in nahezu allen untersuchten Jahren am Standort Elbe / Prossen gefunden) und das mit der höchsten Konzentration vorkommende Rodentizid (Konzentrationen bis ca. 5 µg/kg Frischgewicht am Standort Saar / Rehlingen). Für Bromadiolon, das nur in einigen Jahren nachgewiesen wurde, lag die höchste Konzentration bei ca. 2 µg/kg Frischgewicht (Elbe / Prossen, 2003). Auch Difethialon wurde in Brassenleberproben nur in wenigen Jahren nachgewiesen (Konzentrationen maximal 4 µg/kg Frischgewicht am Standort Saar / Rehlingen 2011).

In einer dritten experimentellen Studie wurden Triclosan und Methyltriclosan in Boden und Regenwurmproben von klärschlammbeaufschlagten landwirtschaftlichen Flächen untersucht. Triclosan gelangt häufig nach der Nutzung mit dem Abwasser in Kläranlagen. In der Kläranlage entsteht neben Abbauprodukten teilweise auch das Transformationsprodukt Methyltriclosan. Ein Teil der Stoffe bindet an Klärschlamm und kann bei dessen Ausbringung als Dünger auf landwirtschaftlichen Flächen in Böden gelangen. Im Rahmen dieser Untersuchung wurde der Oberboden von zwei langjährig mit Klärschlamm behandelten Flächen beprobt und analysiert (oberste Bodenschicht von 20 cm). Es waren Rückstände von ca. 0,5 µg/kg Trockengewicht (TG) Triclosan und ca. 1- 2 µg/kg TG Methyltriclosan nachzuweisen. An einem der Standorte konnten auch Regenwürmer beprobt werden. Die Regenwürmer wiesen eine relativ hohe Triclosankonzentration von ca. 700 µg/kg TG auf. Dagegen lag die Methyltriclosankonzentration unterhalb der Bestimmungsgrenze von 10 µg/kg TG.

Weiterhin wurde im Rahmen des Projekts in der wissenschaftlichen Literatur nach Veröffentlichungen zum Thema Biozidmonitoring gesucht. Die Suche fokussierte auf Publikationen mit Studien aus Europa. Allerdings wurden methodische Publikationen auch aus anderen geografischen Regionen berücksichtigt. Neben wissenschaftlichen Arbeiten wurden auch Berichte von Behörden und Forschungsinstituten zum Thema Biozidmonitoring aufgenommen. Die erstellte Datenbank enthält Informationen zu insgesamt mehr als 200 Studien. Die aus verschiedenen Quellen stammenden Biozidmonitoring-Daten wurden in Bezug auf die untersuchten Wirkstoffe, den Anteil an Proben mit einem Gehalt über der jeweiligen Bestimmungsgrenze (BG), und dem Anteil an Proben mit Konzentrationen über den Effektschwellen (PNECs, oder Umweltqualitätsnormen, UQNs) ausgewertet. Die meisten recherchierten Daten stammen aus dem Oberflächengewässermonitoring (Wasserphase, teilweise Biota oder Schwebstoffe). Die wichtigsten ausgewerteten Datensätze sind: ein größerer Satz Gewässermonitoring-Daten für etwa 20 Biozide, der freundlicherweise vom bayerischen LfU bereitgestellt wurde; aggregierte Datensätze (Fact Sheets) für etwa 10 Biozidwirkstoffe mit Monitoring-Daten aus mehreren europäischen Ländern aus der EMPODAT Datenbank des NORMAN-Netzwerks (hauptsächlich Wasser); Datensätze aus der Flusswassermonitoring-Datenbank der europäischen Umweltagentur (EEA); Schwebstoffmonitoring-Daten für mehrere Biozide aus retrospektiven Analysen von archivierten Proben aus der Umweltprobenbank des Bundes. Die Wasserkonzentrationen lagen für die meisten Biozidwirkstoff unterhalb der jeweiligen BG. Für einige Verbindungen wurden aber auch Überschreitungen der Wirkschwellen beobachtet. Für bestimmte Biozide war die erreichte BG zu hoch (oberhalb der PNEC/UQN), so dass keine Überprüfung von Schwellenwertüberschreitungen möglich war. Wenn die recherchierten Datensätze Zeitreihen enthielten, wurden diese hinsichtlich möglicher Trends ausgewertet, beispielsweise um zu prüfen, ob Änderungen der Umweltkonzentrationen mit Genehmigungsentscheidungen für diese Biozide korrelierten.

Schließlich wurden die recherchierten Biozidmonitoring-Daten für die Validierung des entwickelten Priorisierungsschemas genutzt. Die Priorisierung von Stoffen für das Umweltmonitoring erfolgt in Bezug auf die Relevanz des Auftretens der Stoffe in der Umwelt und die möglicherweise durch einen Stoff verursachten unerwünschten Wirkungen. Es wurde geprüft, ob die Monitoring-Daten die Anwesenheit der priorisierten Verbindungen in den entsprechenden im Priorisierungsschema identifizierten Kompartimenten bestätigen. Hierbei zeigte sich nur eine mäßige Übereinstimmung.

Dieser Befund scheint darin begründet zu sein, dass zum einen aufgrund fehlender EU-Biozid-bewertungsberichte im Priorisierungsschema nicht alle relevanten Biozide berücksichtigt werden konnten. Zum anderen erscheinen die aus den Bewertungsberichten entnommenen Daten nicht immer plausibel. Weiterhin ergab die Auswertung, dass geprüft werden sollte, ob im Priorisierungs-ansatz für bestimmte Biozid-Produktgruppen eine höhere Gewichtung des Eintrags sinnvoller ist, um die Expositionsrelevanz angemessen abzubilden.

Zum Abschluss des Projekts wurden die Ergebnisse im Rahmen eines zweiten, vom Umweltbundes-amt in Zusammenarbeit mit dem NORMAN-Netzwerk organisierten, internationalen Biozidmonito-ring-Workshops im Juni 2015 in Berlin vorgestellt. Mehr als 70 Workshop-Teilnehmer aus mehr als einem Dutzend europäischer Staaten, die Behörden, Forschungsinstitute und Universitäten, Indust-rie und Industrieverbände sowie Nichtregierungsorganisationen repräsentierten, nahmen an den Diskussionen der 13 Vorträge, 13 Poster und drei Arbeitsgruppen teil. Die Diskussionen konzentrier-ten sich insbesondere auf kompartimentspezifische Monitoringansätze und behandelten Aspekte wie Priorisierung, Probenahmeverfahren, Messungen und Datenbanken. Die Präsentationen der Referen-ten sowie der Abschlussbericht mit den Schlussfolgerungen des Workshops sind auf den Internetsei-ten des NORMAN-Netzwerks veröffentlicht (www.norman-network.net/?q=node/202).

Summary

The EU Biocidal Products Regulation (BPR; No. 528/2012) causes changes in the use of biocides and thus of their environmental concentrations. On the one hand, environmental burdens may increase for biocides included in the list of approved substances. On the other hand, a decrease of environmental impacts is expected for compounds subject to non-approval decisions or risk mitigation measures. Environmental monitoring of biocides may help to detect such consequences. Such a monitoring approach would also allow to check whether the environmental concentrations of biocides are above their derived effect thresholds (e.g., predicted no effect concentrations, PNECs). At the moment, however, biocides are not adequately covered in most monitoring programmes. For example water monitoring traditionally covers mainly plant protection products (PPPs; partially also approved as biocides), substances derived from industrial sources and certain ubiquitous pollutants. The aim of this project was to develop a proposal for a comprehensive monitoring concept for biocides. This should allow a better coverage of biocides in existing monitoring programmes in the future.

In November 2012 a first international workshop on environmental monitoring of biocides was organised by the German Environment Agency (UBA) and NORMAN, the European network of reference laboratories and research centres for the monitoring of emerging pollutants (http://www.norman-network.net), to obtain an overview of existing biocidal monitoring activities in Germany and other European countries. The workshop served as a platform to exchange existing information and data on exposure pathways of biocides, to discuss the prioritisation of biocides for future inclusion in monitoring programmes, to address practical issues of sampling and analysis and to debate data processing and analysis of monitoring data of biocides. Important aspects in the field of biocides monitoring were presented and discussed in break-out groups.

As a basis for the implementation of a broad biocides monitoring in Germany, the project optimised a concept for the prioritisation of biocidal compounds for a compartment-specific environmental monitoring. To this end a proposal elaborated in a previous project was developed further. This prioritisation approach covers biocides for which (public or confidential) EU biocide assessment reports are available as the primary data sources. The covered biocides are either currently being assessed in the EU biocides review programme or have already been approved under the EU BPR. The assessment reports often also contain information and data on potential transformation products (TPs). In total about 170 compounds including TPs were considered for the prioritisation approach. The proposed prioritisation scheme consists of several steps. In a first step, the covered substances are assessed regarding their relevance for possible direct or indirect emissions into environmental media. This assessment is mainly based on the purpose of use of a compound in certain biocidal product types and their relevance for emissions into environmental media during usage. In addition, available information on consumption is considered (e.g. operationalised as number of biocidal products with the respective active ingredient registered in Germany). The second step involves the assessment of possible adverse effects of biocidal active substances on the basis of data from the EU biocide assessment reports (e.g., PNECs). In the third step, the relevance of biocides for a monitoring in different environmental compartments is evaluated (e.g., water phase, suspended particulate matter (SPM), biota). During this step substance-specific properties such as the distribution between environmental media, persistence or bioaccumulation potential are considered depending on the respective compartment. Finally, a list of biocides prioritised as relevant has been derived for each compartment.

To prepare the implementation of a comprehensive biocides monitoring concept, information on existing monitoring programmes for relevant environmental compartments in Germany was compiled. Proposals for a possible implementation were elaborated for those compartments that are

currently not subject to monitoring programmes. Data cover information on sampling and analytical methods (including quality assurance aspects). Information is now available for the following environmental compartments: surface water (water phase, SPM / sediment, biota), terrestrial ecosystems (soil, biota, and groundwater), sewage treatment plants (effluents, sewage sludge), and atmosphere. For these compartments results from the prioritisation approach are also available. The compiled information will be made available for monitoring institutions. For better coverage of biocides in surface water monitoring it is recommended to collaborate with the agencies of the federal states which operate the Water Framework Directive (WFD) monitoring. In order to allow even a retrospective tracking of biocide changes the use of material from environmental specimen banks (ESBs) is proposed. Archived biota samples (e.g., fish or raptor tissue) may be used to identify trends of non-polar biocides. Polar substances may be analysed in archived SPM from rivers (case studies are available). Special aspects may be investigated in snapshot monitoring studies (e.g., antifouling agents in marinas). For soil monitoring collaboration with the federal states is also suggested. The federal states operate long-term soil monitoring sites. In this area research projects for the monitoring of a set of relevant compounds appear to be most suitable, for example, for the investigation of biocides in soils on which manure or sewage sludge have been spread.

For the assessment of monitoring data it has to be examined in each case whether the active ingredients are also used under other regulations (e.g., as PPPs). In these cases, it is often not possible to assign the environmental findings to a specific usage. Consequently, environmental monitoring mainly focuses on substances that are only approved as biocides. As an alternative, certain sampling strategies may be applied to detect selectively possible biocide inputs (e.g., investigations in certain seasons when no application of PPPs is expected or in urban areas where the use of the respective compounds as PPPs is not expected).

In an experimental project section exemplary investigations were carried out on the occurrence of relevant biocides in different environmental media. The aim of a first experimental study was to develop and validate a simple multi-parameter method for the analysis of a set of biocides in different environmental compartments (wastewater, surface water and sewage sludge). For the investigation of selected samples a set of eight target analytes was determined: triclosan (an antibacterial substance for which a non-approval decision as a disinfectant has been adopted recently), methyltriclosan (transformation product of triclosan), cybutryne (Irgarol) and the azole fungicides propiconazole, tebuconazole, imazalil, thiabendazole and cyproconazole. Samplings were performed in seven German sewage treatment plants and their corresponding receiving waters at two times. The sensitivity of the analytical methodology was characterized by means of the respective substance-specific limits of quantification (LOQs) which were compared to the estimated effect thresholds (PNECs). The analysed samples revealed only sporadic burdens with the target analytes. Five azole fungicides and methyltriclosan were detected in wastewater and surface water samples. One azole fungicide (cyproconazole) was identified in sewage sludge samples. Generally, target analyte burdens were more dominant in the water samples than in the sludge samples.

In a second experimental study eight rodenticides (anticoagulants) were investigated in fish. In several bream liver samples from 17 different locations in Germany retrieved from the archive of the German ESB bromadiolone, brodifacoum and difethialone were detected at concentrations above the LOQs. Based on the results from the spatial comparison samples from the sites Saar / Rehlingen and Elbe / Prossen were selected for a temporal comparison. From both sites ten bream liver samples from the ESB archive were analysed retrospectively (period 1992-2013). The results reveal no clear concentration trends, but changes of rodenticide burdens from year to year. Brodifacoum was the most often detected active ingredient (found in almost all years examined at the site Elbe / Prossen) and occurred with the highest levels (up to 5 µg/kg wet weight at the site Saar / Rehlingen). For bromadiolone, which was detected only in a few years, the highest concentration was about 2 µg/kg wet weight (site Elbe / Prossen, 2003). Difethialone, too, was detected in bream liver samples in a few years only (up to 4 µg/kg wet weight at the site Saar / Rehlingen 2011).

In a third experimental investigation triclosan and methyltriclosan were analysed in soil and earthworm samples of sewage sludge-treated agricultural soils. After use, triclosan reaches sewage treatment plants. During the degradation process in the treatment plant triclosan is partly transformed into the transformation product methyltriclosan. A fraction of the compounds binds to sewage sludge which may reach agricultural soils when applied as a fertilizer. In this study, the top soil from two sites which were treated for many years with sewage sludge was sampled and analysed (top soil layer of 20 cm). In the soils residues of about 0.5 µg/kg dry weight triclosan and 1 - 2 µg/kg dry weight methyltriclosan were detected. At one of the sites also earthworms could be sampled. The earthworms had a relatively high level of triclosan of about 700 mg/kg dry weight. In contrast, the methyltriclosan concentration in the earthworms was below the LOQ of 10 µg/kg dry weight.

Furthermore, the scientific literature was searched for publications regarding biocides monitoring during the course of the project. The search mainly focused on publications covering studies from Europe. However, methodological publications from other geographical regions have been considered, too. Besides scientific papers also reports on biocides monitoring from public agencies and research institutes have been covered. The database contains descriptions from more than 200 studies. The biocides monitoring data compiled from various sources were evaluated with respect to the tested biocidal compounds, the fraction of samples with levels above the respective LOQ, and the fraction of samples with concentrations above the effect threshold (PNECs or environmental quality standards, EQSs). Most of the gathered data are from monitoring of surface waters (water phase, partially biota or SPM). The most relevant records evaluated were: a larger set of surface water monitoring data for about 20 biocides which was kindly provided by the Bavarian LfU; aggregated records (fact sheets) for about 10 biocides with monitoring data from several European countries from the EMPODAT database of the NORMAN network (data mainly from water monitoring); data sets from the river water monitoring database of the European Environment Agency (EEA); retrospective monitoring data for several biocides in SPM samples retrieved from the German ESB archive. Water concentrations were below the respective LOQs for most biocides. However, for some biocides the effect thresholds were exceeded. For certain biocides the applied LOQ was too high (above PNEC / EQS) so that an assessment of possible threshold violations was impossible. If the compiled records contained time series evaluations for possible trends were performed. Thus it was tested, for example, whether changes in environmental concentrations correlated with approval or non-approval decisions of these biocides.

Finally, the compiled biocides monitoring data were used for the validation of the proposed prioritisation scheme. The prioritisation of biocides for the environmental monitoring is carried out with respect to the relevance of the occurrence of a substance in the environment and possible adverse effects caused. It was examined whether the monitoring data confirm the presence of the prioritised compounds in the respective compartments identified in the prioritisation approach. Here, only a moderate agreement was found. On the one hand, this may be due to the fact that not all relevant biocides could be covered in the prioritisation approach due to the lack of EU biocide assessment reports. On the other hand, data taken from the assessment reports did not always appear plausible. The evaluation also revealed that it should be examined whether a higher weighting of the relevance of an environmental exposure in the prioritisation approach for certain biocidal product types could improve the results.

At the end of the project results were presented during a second international workshop on biocides monitoring organised again by the German Environment Agency in collaboration with the NORMAN network in June 2015 in Berlin. More than 70 workshop participants from more than a dozen European countries representing national agencies, research institutes and universities, industry and industry associations as well as non-governmental organisations took part in the discussions around 13 presentations, 13 posters and three break-out groups. Discussions particularly focused on compartment-specific monitoring approaches and covered aspects such as prioritisation, sampling methods, measurements and databases. The presentations of the speakers and the final report with the conclusions of the workshop are publically available on the website of the NORMAN network (www.norman-network.net/?q=node/202).

1 Introduction

The European Directive 98/8/EC (Biocidal Product Directive, BPD; EC 1998) on placing biocidal products on the market was adopted in 1998 and subsequently transposed into national law by the EU member states. It was replaced by EU regulation No 528/2012 (Biocidal Products Regulation, BPR; EU 2012) by September 1, 2013.

Up to now, about 90 biocidal active substances have been authorised under the BPD (positive list in Annex I/Ia) or the BPR (list of approved substances; http://echa.europa.eu/information-on-chemicals/biocidal-active-substances), but many biocidal substances are still under assessment (biocide review programme according to Regulation (EU) No 1062/2014; EU 2014) for at least one biocidal product type (PT).

The implementation of the BPD has already caused a change in the use of biocidal active substances in Europe. Some substances have been withdrawn from the market, or will be withdrawn soon as a consequence of non-approval decisions. Additionally, the use of certain biocidal substances will be restricted by risk mitigation measures.

Environmental monitoring can help in assessing whether the implementation of the BPD has positive effects on the environmental quality, whether there is a risk, and whether the exposure estimations applied for risk assessment are realistic. Thus it may be possible to answer questions like: Are lower environmental concentrations of biocides detected in recent years? Are the measured concentrations below the derived PNEC? Are the modelling results for biocides consistent with the monitoring data?

2 1st Workshop on biocides monitoring (Berlin, November 2012)

A first international workshop on biocides monitoring was held jointly by the German Environment Agency (Umweltbundesamt) and NORMAN, the European network of reference laboratories and research centres for monitoring emerging environmental pollutants (http://www.norman-network.net). The workshop in Berlin in November 2012 served as a platform to exchange existing information and data on exposure pathways for biocides, prioritisation of biocides for inclusion in future monitoring programmes, practical issues regarding sampling and analysis, and monitoring data handling and evaluation. 65 experts from 11 EU member states representing research, government agencies, consultants and industry participated in the workshop. In addition to 18 oral presentations, 11 posters were exhibited.

The workshop report is attached as a separate document (Annex 1; Jäger et al. 2013). The documentation including the presentations is available on the NORMAN website (www.norman-network.net/?q=node/99).

3 Literature compilation on biocides monitoring

3.1 Databank with references on publications on biocides monitoring

The scientific literature was searched for publications on biocides monitoring. The search was focused on papers with studies from Europe. However, methodological publications were also covered from other geographic regions. Beside scientific papers also reports from government agencies and research institutes were considered. In total, more than 200 citations were covered.

Table 1 gives an overview of matrices frequently investigated for biocides and examples for biocidal compounds covered. Countries often covered in studies are Spain, Sweden, Norway, United Kingdom, Germany, France, Austria and Italy.

Table 1: Overview of literature regarding biocides monitoring data.

Matrix	No. of publications/reports	Examples for biocides covered in the investigations
Surface water	ca. 60	Triclosan, cybutryne (Irgarol), diuron#, carbendazim#, DEET, tolylfluanid#, quaternary ammonium compounds
Freshwater sediment and suspended particulate matter (SPM)	ca. 20	Triclosan/methyltriclosan, triclocarban, cybutryne (Irgarol), tebuconazole#, propiconazole#, quaternary ammonium compounds
Freshwater fish	ca. 15	Triclosan/methyltriclosan, tributyltin, (former biocide), isoproturon, pyrethroids
Marine water	ca. 35	Cybutryne (Irgarol), diuron, dichlofluanid, TBT (former biocide), transformation products
Marine sediment	ca. 25	Antifouling biocides: TBT (former biocide), cybutryne (Irgarol), diuron, dichlofluanid
Passive samplers	ca. 5	Triclosan, tebuconazole#, propiconazole#, chlorotoluron#, terbuthylazine#, cybutryne (Irgarol), DEET, imidacloprid#, cypermethrin#, deltamethrin#
Wastewater	ca. 20	Triclosan, terbuthylazine#, diuron#, tebuconazole#, propiconazole#, Brodifacoum#, DEET, cypermethrin#, bromadiolone#, difenacoum#, chlorophacinone
Sewage sludge	ca. 20	Triclosan, carbendazim#, diuron#, cybutryne (Irgarol), permethrin, quaternary ammonium compounds
Sewage treatment plants effluents	ca. 25	Diuron#, DEET, terbuthylazine#, triclosan/ methyltriclosan, terbutryn#, tebuconazole#, propiconazole#, quaternary ammonium compounds
Storm water	ca. 3	Carbendazim#, BIT, terbutryn#, cybutryne (Irgarol), diuron#, isoproturon, tebuconazole#, propiconazole#, IPBC, DCOIT, cypermethrin#
Soil	ca. 5	Fipronil# and transformation products, tolylfluanid, tebuconazole#, propiconazole#, carbendazim#, brodifacoum#, bromadiolone#, difenacoum#, chlorophacinone
Terrestrial biota (e.g., rodents, raptors)	ca. 25	Brodifacoum#, bromadiolone#, difenacoum#, chlorophacinone
Groundwater	ca. 10	Carbendazim#, imidacloprid#, tebuconazole#, diuron#, isoproturon#, terbutryn, transformation products

compound is or was also approved as plant protection product so that the source is not clearly allocable.

In a separate document, provided in digital form, information on the retrieved studies is compiled. For each study beside the abstract also covered biocides and matrices are listed (Compilation of biocides monitoring publications, October 2015; pdf-file, internal document, not to be published). Beside publications/reports with environmental monitoring data also several review studies are covered in the database as well as reports describing mainly analytical methods without relevant monitoring data.

3.2 Monitoring data compilation

Monitoring data from the most relevant scientific publications and reports were compiled in a Microsoft Excel file template provided by UBA. In this file about 800 data sets from about 20 studies are gathered. Examples for compounds/matrices combinations covered are: 3-iodo-2-propynylbutylcarbamate (IPBC), cybutryne (Irgarol), diuron, isoproturon, propiconazole, terbutryn, tebuconazole, and brodifacoum in STP influents; cybutryne (Irgarol), isoproturon, DEET, diuron, terbutryn, and terbuthylazine in STP effluents; triclosan in sewage sludge; acetamiprid, carbendazim, chlorotoluron, cybutryne (Irgarol), diuron, DEET, imidacloprid, isoproturon, propiconazole, terbutryn, thiabendazole, tebuconazole, and thiacloprid in surface water; cybutryne (Irgarol) and propiconazole in SPM.

In addition data on biocides were retrieved from the Waterbase - Rivers data base available at the website of the European Environment Agency (EEA 2014). This database contains water phase monitoring data from EU member states obtained from monitoring in the context of the Water Framework Directive (WFD). Beside WFD priority substances also additional compounds are covered (e.g., compounds identified as national priority substances or water basin-specific pollutants). About 70,000 relevant data sets were selected. Additional information on the EEA data set regarding covered biocides and first evaluations are presented in Annex 7 (“Evaluation of monitoring data and application for the validation of the proposed concepts for the prioritisation and monitoring of biocides”, Rüdel 2015).

The Microsoft Excel file with monitoring data is provided in digital format (Compilation of biocides monitoring data, October 2015; internal Excel file, not to be published).

4 Optimisation of the previously proposed prioritisation approach

In this project phase a concept for the prioritisation of biocidal substances for an environmental monitoring was optimised. The set of covered biocides included compounds for which (public or confidential) EU biocide assessment reports as primary data source were available. These biocides are either in the EU biocides review programme or already approved according to the EU BPD (EU 2012). Often also data on potential transformation products (TPs) are given in the assessment reports. In total about 170 compounds including TPs were covered by the prioritisation approach. The proposed prioritisation scheme consists of several steps. In a first step compounds are evaluated for potential direct or indirect emissions into environmental media (mainly based on the intended use in certain biocide product types and their relevance for environmental media). Additionally, available information on consumption, operationalised, e.g. as number of registered products with the respective biocide in Germany, is applied. The second step covers the assessment of the potential to cause adverse effects based on data available from the assessment reports (e.g., PNECs). In a third step the relevance of biocides for monitoring in an environmental compartment (e.g., water phase, SPM, biota) is scored. Depending on the compartment, substance-specific properties relevant for partitioning between compartments, persistence and/or bioaccumulation potential are considered. Finally, for each compartment a list of prioritised biocides was derived. The final compartment-specific prioritisation lists are discussed with regard to available biocides monitoring data. In the assessment of monitoring data it has also to be considered whether the compounds are applied under other regulations, too (e.g., as PPPs). In these cases it is often not possible to allocate environmental findings to a specific usage. Consequently, the evaluation has to focus primarily on monitoring data of compounds solely approved as biocides.

The report on the optimisation of the prioritisation approach and the final compartment-specific ranking lists is attached as a separate document (Annex 2; German language report “Überprüfung, Überarbeitung und Vervollständigung des vorläufigen Priorisierungs-/Monitoring-Konzepts”, Rüdel and Fliedner 2014a).

5 Design of a Biocides Monitoring Programme

The BPD (EU 2012) causes changes of the use of biocides and consequently of their environmental concentrations. Such consequences may be proven by an environmental monitoring. However, in most monitoring programmes biocides are not appropriately covered. Traditionally, e.g., in surface waters mainly PPPs (partly also approved as biocides), compounds from industrial sources and legacy chemicals are monitored. This project phase aimed to propose a comprehensive monitoring concept for biocides. Main purpose of this approach is to achieve a better coverage of biocides in existing monitoring programmes. As a first step, relevant compartments were identified and relevant biocides prioritised. These lists can be provided to interested monitoring authorities. For the better coverage of biocides in surface water monitoring, cooperation with the German federal states which operate the WFD monitoring is recommended. To allow also a retrospective tracking of changes, the utilisation of samples from existing environmental specimen banks is suggested. Archived biota samples (e.g., fish or raptor tissues) may be used to identify trends of non-polar biocides. For more polar compounds archived SPM from rivers may be analysed (case studies already available). Special aspects may be investigated in a snapshot monitoring (e.g., antifouling biocides in marinas). For soil monitoring, collaboration with federal states which operate permanent soil investigation sites is recommended. In this area research projects seem most appropriate, for example for investigating biocides on sites with liquid manure or sewage sludge spreading.

The report on the proposed monitoring approach is attached as a separate document (Annex 3; “Design of a Biocide Monitoring Programme”, Rüdel and Fliedner 2014b).

6 Analyses of selected biocides as candidates for monitoring measures

6.1 Monitoring of triclosan, methyltriclosan and azole fungicides in STPs and receiving waters

The objective within this project phase was to work out and validate a simple multi-parameter method for the analyses of biocides in abiotic matrices of various environmental compartments (wastewater, surface water and sewage sludge) for monitoring measurements. Eight target substances were defined for analysing selected sample sets. The group of target analytes comprised triclosan, methyltriclosan (transformation product of triclosan), cybutryne (Irgarol) and the azole fungicides propiconazole, tebuconazole, imazalil, thiabendazole and cyproconazole. Sampling took place in seven German urban sewage treatment plants (STPs) and their corresponding receiving waters during two sampling campaigns. Water samples from STPs and receiving waters were extracted using solid phase extraction (SPE) according to Wick et al. (2010). Sewage sludge samples were extracted by accelerated solvent extraction (ASE) and subsequent fractionation and analysis by gas chromatographic-mass spectrometric methods (GC/MS) were performed. The analytical method has been checked to have sufficient sensitivity by comparison of the limits of quantification (LOQs) for GC/MS analyses to the predicted no effect concentrations (PNECs). For quality assurance purposes recovery rates have been determined. Deuterated substances used as internal standards could be recovered successfully. Matrix effects were decreased by optimizing extraction methods as well as instrumental settings and conditions. Details of the extraction methods are described in standard operating procedures (SOPs). The developed multi-parameter method allows the reproducible analysis of all target biocides in waters at levels in the range or even below the derived PNECs as well as in sewage sludge extracts.

The investigated sample sets document a sporadically contamination by the target analytes. Five azole fungicides and methyltriclosan were detectable in wastewater and receiving water samples from the investigated STPs. One azole fungicide (cyproconazole) was detectable in sewage sludge. The contamination of target analytes was more dominant in the water phase than in sewage sludge.

The report is confidential since it contains detailed information on the investigated treatment plants. A publication is only possible after anonymisation of the sites information. The report is attached as a separate document (Annex 4 - CONFIDENTIAL; “Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measures”, Schwarzbauer and Wluka 2015). A publication draft by Wluka et al. with the title “Analytical method development for the determination of eight biocides in various environmental compartments and application for monitoring purposes” was submitted to a peer-reviewed journal.

6.2 Retrospective monitoring of rodenticides in archived freshwater fish

For the determination of eight rodenticides in fish muscle and liver an appropriate method was adapted. Initial analyses revealed that higher concentrations were detectable in fish liver as compared to fish filet. Thus the method was further optimised for liver samples and validated. The final protocol applied high-resolution mass spectrometric detection after liquid chromatography separation and yielded a limit of quantification (LOQ) of 0.06 µg/kg wet weight for most compounds (validated by repeated measurements of spiked samples). Applying the final method to bream liver samples from the German Environmental Specimen Bank (ESB), bromadiolone, flocoumafen, brodifacoum, and difethialone were found at levels above the LOQs. In a further step, bream liver samples from the ESB archive sampled at 17 sites across Germany were analysed retrospectively. In this spatial comparison for the year 2011, highest levels were found at the site Saar / Rehlingen: 0.8 µg/kg bromadiolone, 4.6 µg/kg brodifacoum, 4.0 µg/kg difethialone. These three compounds were the only identified rodenticides. Brodifacoum was the most frequently detected rodenticide at all test sites (found at 10 of 17 sites). The other rodenticides occurred less frequently (bromadiolone at 3, difethialone at 7 locations). Difethialone reached a concentration of 4.0 µg/kg in bream liver from the site Saar / Rehlingen. Based on the results of the rodenticide spatial screening, samples from Saar / Rehlingen and Elbe / Prossen were chosen for a temporal comparison. From both sites, ten bream liver samples from the ESB archive were retrospectively analysed (years 1992 to 2013). Examining the results, no clear trend can be observed, but year-to-year changes in rodenticide loads. Again, brodifacoum was the most frequently detected rodenticide (detected in almost every investigated year at Elbe / Prossen), and the most abundant one (levels of up to 4.6 µg/kg wet weight at the site Saar / Rehlingen 2011). Bromadiolone (up to 1.8 µg/kg wet weight, Elbe / Prossen 2003) and difethialone (up to 4.0 µg/kg wet weight, Saar / Rehlingen 2011) were detected only in some years in bream liver.

A detailed report including the method description and the analytical data is attached as a separate document (Annex 5 - CONFIDENTIAL; “Determination of Rodenticides in Fish Samples of the German Environmental Specimen Bank”, Kotthoff et al. 2015). The publication of the results in a peer-reviewed journal is in preparation.

6.3 Triclosan and methyltriclosan in soil and earthworm samples from sewage-sludge applied fields

Triclosan is an antibacterial agent and is included in the EU biocides review programme. The risk assessment for the use as a biocide in product type 1 (disinfectants) was finalised recently and a non-approval decision has been adopted. Additionally triclosan is also used as cosmetics ingredient. After use triclosan reaches sewage treatment plants with the wastewater. During sewage treatment the transformation product methyltriclosan is formed. During treatment, a part of the triclosan and methyltriclosan is bound to sewage sludge and may reach soil if sewage sludge is spread as fertilizer on agricultural land. In this study top soil from two long-term sewage sludge-treated sites in Lower Saxony (Germany) was sampled and analysed for triclosan and methyltriclosan (upper 20 cm soil layer). Residues of 0.5 and 0.3 µg/kg dry weight (dw) triclosan and 0.8 and 1.6 µg/kg dw methyltriclosan could be detected (limits of quantification < 0.1 µg/kg dw for both compounds). At one of the sites also earthworms could be sampled. The earthworms had a relatively high triclosan concentration of 670 µg/kg dw. Methyltriclosan, on the other hand, was just detectable at a concentration of about 6 µg/kg dw (value only indicative, since below the limit of quantification of 10 µg/kg dw). The factor for the enrichment from soil to earthworm was 1500 for triclosan and about 7 for methyltriclosan. Exemplarily analysed earthworm samples from one agricultural and four forest sites retrieved from the stock of the German environmental specimen bank contained only small amounts of triclosan (below the limit of detection), but no traces of methyltriclosan.

The study is described in detail in a report which is attached as a separate document (Annex 6 - CONFIDENTIAL; “Determination of triclosan and methyl-triclosan in soil and earthworm samples from sewage sludge-treated agricultural sites”, Kharel et al. 2015). A draft paper for the submission to a peer-reviewed journal has been prepared.

7 Evaluation of monitoring data and application for the validation of the proposed concepts for the prioritisation and monitoring of biocides

Biocides monitoring data from several sources were retrieved and evaluated regarding the covered compounds, the fraction of samples with levels above the respective LOQ, and the fraction of samples with concentrations exceeding effect levels (PNECs, or environmental quality standards, EQSs). Retrieved data were mainly from surface water monitoring (water phase, partly biota or SPM). The main data sets evaluated were: a larger surface water data set with biocides monitoring data for about 20 compounds kindly provided by the Bavarian Environment Agency (LfU); aggregated data sets (fact sheets) for about 10 biocidal compounds with relevant monitoring data from several European countries retrieved from the EMPODAT data base of the NORMAN association (mainly water monitoring data); data sets from the European Environment Agency (EEA) river water monitoring data base; SPM monitoring data for several biocides from retrospective analysis of archived samples from the German Environmental Specimen Bank. The water phase concentrations for most of the biocides were often below the respective LOQ. However, for some compounds also exceedance of the effect thresholds was observed. For certain biocides the applied LOQ was too high (above the PNEC/ EQS) to allow checking the exceedance of effect levels. If the retrieved data sets contained time series these were evaluated for possible trends, e.g., to prove whether changes in environmental concentrations were correlated with approval decisions for these biocides. Finally the available biocides monitoring data were applied for the validation of a previously developed prioritisation concept for biocides. The prioritisation is based on the relevance of a chemical for occurring in the environment and causing adverse effects. It was assessed whether the monitoring data are confirming the presence of the prioritised compounds in the respective compartments identified in the prioritisation approach.

The report is attached as a separate document (Annex 7; "Evaluation of monitoring data and application for the validation of the proposed concepts for the prioritisation and monitoring of biocides", Rüdel 2015).

8 2nd Workshop on biocides monitoring (Berlin, June 2015)

The German Environment Agency (UBA) organised in collaboration with the NORMAN network a second international workshop on biocides monitoring in Berlin in June 2015. The discussions focused especially on compartment-specific monitoring approaches and covered aspects like prioritisation, sampling strategies, measurements and data bases. More than 70 workshop attendees from more than a dozen European countries representing authorities, research institutes and universities, industry and industry associations as well as non-governmental organisations participated in the discussions of 13 oral presentations, 13 posters and three break-out groups.

The main conclusions summarized in the workshop closing session are:

- Generally, a deficit was seen in the biocides risk assessment since the focus of the authorisation procedure is on single products while the overall exposure from different products / different uses is not covered appropriately; to this end environmental monitoring could inform the risk assessment process with aggregated exposure data.
- Up to now biocides are not adequately considered in monitoring programmes (as compared, e.g., to active ingredients applied as PPPs); available monitoring data mainly cover surface waters while findings for soil and groundwater are almost totally absent for biocides.
- The necessity of the availability of consumption data for biocides as an important input to prioritisation approaches was emphasized; additional reporting requirements (analogously to PPPs for which the regulation concerning statistics on pesticides is applied) would be a possibility to address the lack of data on biocides production and usage volumes.
- A new finding presented during the workshop was that rodenticides (anticoagulants) were detected as emerging contaminants in urban aqueous systems; until now the focus of rodenticides monitoring has been mainly on the terrestrial compartment where these compounds were detected in non-target organisms.
- In addition to surface waters, in urban environments storm water containing, e.g., preservatives leached from building facades was identified as relevant matrix for the monitoring of biocides.
- Some biocidal compounds are difficult to quantify at relevant concentrations in environmental compartments; for biocides such as pyrethroids, for example, improvements of the analytical methods are urgently required since the derived effect thresholds (PNECs or environmental quality standards) are below current LOQs.

A separate report documents the workshop discussions and abstracts of the contributions as well as the main conclusions drawn (Annex 8; workshop report "Environmental monitoring of biocides in Europe – compartment-specific strategies", Pohl et al. 2015). The documentation including the presentations is available on the NORMAN website (www.norman-network.net/?q=node/202).

9 References

EC (1998): Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market (Biocidal Products Directive). OJ L 123, 24.4.1998, p. 1-63. http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1444926747317&uri=CELEX:31998L0008

EEA (2014): Waterbase - Rivers, v14. Microsoft Access File. European Environment Agency (EEA), Copenhagen, Denmark. www.eea.europa.eu/data-and-maps/data/waterbase-rivers-10

EU (2012): Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products (Biocidal Products Regulation). OJ L 167, 27.6.2012, p. 1-123. http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1444926747317&uri=CELEX:32012R0528

EU (2014): Commission Delegated Regulation (EU) No 1062/2014 of 4 August 2014 on the work programme for the systematic examination of all existing active substances contained in biocidal products referred to in Regulation (EU) No 528/2012 of the European Parliament and of the Council. OJ L 294, 10.10.2014, p. 1-34. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32014R1062

Jäger S, Dulio V, Schwarzbauer J, Slobodnik J, Rüdel H (2013): Environmental monitoring of biocides in Europe - from prioritisation to measurements. Workshop Report (November 5-6, 2012 in Berlin). Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany. Sub-report (Annex 1) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Kotthoff M, Jürling H, Bücking M, Rüdel H (2015): Determination of Rodenticides in Fish Samples of the German Environmental Specimen Bank. Sub-report (Annex 5) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Pohl P, Dulio V, Botta F, Schwarzbauer J, Rüdel H (2015): Environmental monitoring of biocides in Europe - compartment-specific strategies. Workshop Report (June 25-26, 2015 in Berlin). Sub-report (Annex 8) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Rüdel H (2015): Evaluation of monitoring data and application for the validation of the proposed concepts for the prioritisation and monitoring of biocides. Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany. Sub-report (Annex 7) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Rüdel H, Fliedner A (2014a): Überprüfung, Überarbeitung und Vervollständigung des vorläufigen Priorisierungs-/Monitoring-Konzepts. Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany. Sub-report (Annex 2) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Rüdel H, Fliedner A (2014b): Design of a Biocide Monitoring Programme. Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany. Sub-report (Annex 3) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Schwarzbauer J, Wluka A (2015): Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measures. EMR Energy & Mineral Resources Group, Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Aachen, Germany. Sub-report (Annex 4) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Kharel S, Kotthoff M, Rüdel H (2015): Determination of triclosan and methyl-triclosan in soil and earthworm samples from sewage sludge-treated agricultural sites. Sub-report (Annex 6) on project (FKZ) 3712 67 403 “Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment” on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Appendix

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Annex 2: Optimisation of the biocides monitoring prioritisation approach (in German language)

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Environmental Research
of the Federal Ministry for the Environment,
Nature Conversation and Nuclear Safety

Project no. (FKZ) 3712 67 403
UBA-FB-00

Environmental monitoring of biocides in Europe – from prioritisation to measurements
Workshop Report, November 5–6, 2012 in Berlin (Annex 1)

by

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On behalf of Umweltbundesamt, Dessau-Rosslau, Germany

January 2013

Kurzbeschreibung

Dieser erste internationale Workshop zum Umweltmonitoring von Bioziden wurde gemeinsam vom Umweltbundesamt (UBA) und NORMAN, dem europäischen Netzwerk von Referenzlaboratorien und Forschungszentren für das Monitoring von Neuen Umweltschadstoffen (http://www.norman-network.net) veranstaltet. Der Workshop diente als Plattform, um vorhandene Informationen und Daten zu Expositionspfaden von Bioziden auszutauschen, die Priorisierung von Bioziden für die zukünftige Aufnahme in Monitoringprogramme zu diskutieren, praktische Fragen der Probenahme und Analyse zu behandeln sowie die Datenverarbeitung und Auswertung von Monitoringdaten von Biozi-den zu erörtern. 65 Experten und Expertinnen aus 11 EU-Mitgliedstaaten, die Forschung, Behörden, Beratungsunternehmen und Industrie repräsentierten, nahmen am Workshop teil. Neben 18 Vorträgen wurden 11 Poster präsentiert. Wichtige Themenkomplexe auf dem Gebiet des Biozidmonitorings wurden vorgestellt und in Arbeitsgruppen diskutiert. Die Workshop-Ergebnisse bilden die Grundlage zur Integration des Biozidmonitoring in das Routine-Umweltmonitoring in Europa.

Abstract

This first international workshop on biocide monitoring was held jointly by the German Federal Environment Agency (Umweltbundesamt, UBA) and NORMAN, the European network of reference laboratories and research centres for monitoring emerging environmental pollutants (http://www.norman-network.net). The workshop served as a platform to exchange existing information and data on exposure pathways for biocides, prioritisation of biocides for inclusion in future monitoring programmes, practical issues regarding sampling and analysis, and monitoring data handling and evaluation. 65 experts from 11 EU member states representing research, government agencies, consultants and industry participated in the workshop. In addition to 18 oral presentations, 11 posters were presented. Important topics in the field of biocides monitoring were presented and discussed in break-out groups. The workshop results are the basis for the future integration of a biocide monitoring into the routine environmental monitoring in Europe.

Contents

Abbreviations

BPD	Biocidal Product Directive (98/8/EC)
DEET	N,N-diethylmetatoluamide
ESB	environmental specimen bank
EU	European Union
GC/MS	gas chromatography-mass spectrometry coupling
LC/MS	liquid chromatography-mass spectrometry coupling
LOD	limit of detection
LOQ	limit of quantitation
NORMAN	European network of reference laboratories and research centres for monitoring emerging environmental pollutants
PNEC	predicted no effect concentration
PPP	plant protection product
REACh	Registration, Evaluation, Authorisation and restriction of Chemicals (EU chemicals management regulation)
SOP	standard operating procedure
STP	sewage treatment plant
UBA	Umweltbundesamt (German Federal Environment Agency)

1 Introduction

The European Biocidal Product Directive 98/8/EC (BPD) on placing biocidal products on the market was adopted in 1998 and subsequently transposed into national law by the EU member states. It will be replaced by EU regulation No 528/2012 which will be applied from September 1, 2013. Some biocidal active substances have already been authorised under the BPD (positive list in Annex I/Ia), but many of the substances are still under assessment (biocide review programme). The implementation of the BPD has already caused a change in the use of biocidal active substances in Europe. Some substances have been withdrawn from the market, or will be withdrawn soon as a consequence of non-inclusion decisions. Additionally, the use of certain biocidal substances will be restricted by risk mitigation schemes.

Environmental monitoring can help in assessing whether the implementation of the BPD has positive effects on the environmental quality (Are lower concentrations detected in recent years?), whether there is a risk (Are the measured environmental concentrations below the derived PNEC?), and whether the exposure estimations applied for risk assessment are realistic (Are the modelling results consistent with the monitoring data?).

This international workshop was held jointly by the German Federal Environment Agency (Umweltbundesamt, UBA) and NORMAN, the European network of reference laboratories and research centres for monitoring emerging environmental pollutants (http://www.norman-network.net). The workshop served as a platform to exchange existing information and data on exposure pathways for biocides, prioritisation of biocides for inclusion in future monitoring programmes, practical issues regarding sampling and analysis, and monitoring data handling and evaluation. 65 experts from 11 EU member states representing research, government agencies, consultants and industry participated in the workshop. In addition to 18 oral presentations, 11 posters were exhibited.

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2 Session reports

On behalf of the Umweltbundesamt Petra Greiner, head of Department IV 1 "International Aspects, Pesticides", welcomed all participants to the workshop on "Environmental monitoring of biocides in Europe" and acknowledged the cooperation with the NORMAN network on this occasion. Ms Greiner emphasised that environmental monitoring can have an impact and illustrated this with the example of the tributyltin compounds. A ban on the use of these compounds as antifouling agents was enacted by a European directive after monitoring data had revealed high burdens in samples from marine sites. By organising this workshop the Umweltbundesamt intended to foster the exchange of experiences from biocide monitoring in Europe and to lay the ground for a common strategy on the use of monitoring data in this field.

In her contribution to the Introduction session, Ingrid Nöh (Umweltbundesamt) described why biocide monitoring seems necessary from the viewpoint of regulatory practice. Since the EU Biocidal Product Directive (BPD) 98/8/EC was enacted in 1998, the use of active substances has changed. A number of biocides will no longer be marketed and may be substituted by other compounds. It is estimated that from about 370 biocides which are reviewed for the BPD, only about 270 will be authorised. Monitoring data can be one tool to ensure a realistic estimation of the environmental exposure by biocides, which is a prerequisite for an effective and realistic environmental risk assessment in biocide regulation (check of exposure models). Environmental monitoring also allows the checking of the effectiveness of risk mitigation measures implemented for biocides. One obstacle for monitoring is the use of substances under different regulations (e.g., as a plant protection product (PPP) and biocide) which often makes it difficult to allocate the source of environmental occurrences of these compounds. In the discussion Ms Nöh explained that the Umweltbundesamt will not build up an own biocide monitoring but intends to cooperate with the monitoring institutions of the federal states.

The NORMAN network was introduced by Valeria Dulio (NORMAN). NORMAN is an independent forum of more than 50 reference laboratories, research centres and related organisations which serves as an interface organisation between science and government. The mission of NORMAN is to exchange information on emerging substances, improve data quality and comparability, and promote synergies among research teams. One activity of NORMAN is the compilation of a list of emerging substances, which includes biocides and PPP. NORMAN also operates the online database EMPODAT on environmental monitoring data for emerging substances (see also contribution by Slobodnik). NORMAN has recently developed a prioritisation scheme specifically designed for emerging substances and associated knowledge gaps. Based on this scheme, a prioritisation exercise is currently being performed in order to identify emerging substances for priority attention, including priority needs for improving existing monitoring data in the aquatic environment, analytical methods, biological tests etc. The prioritisation scheme is based on substance properties, the ecotoxicological relevance of the compounds, and their occurrence in the environment. QSAR and read-across methods are partly applied for the assessment.

The session on general aspects of (biocide) monitoring was introduced by Angelika Steinborn (German Federal Institute for Risk Assessment, BfR) with a talk on analytical methods for monitoring of biocides in the environment. Ms Steinborn discussed whether the data requirements for residue analysis of biocides (e.g., in environmental matrices, body fluids and tissues) are sufficient. An important aspect is which compounds actually form the relevant residue of a biocidal product (e.g., in case of multi-component mixtures such as Margosa extract or substances which form persistent transformation products) and which are the relevant environmental media to be analysed for the respective biocide. Relevant method performance information is recovery rate, precision data, calibration lines, blank values, limit of quantification, and example chromatograms. Information on method requirements and validation is available in the "EU Guidance on Data Requirements for Active Substances and Biocidal Products" and additional "Technical Notes for Guidance on Data Requirements" regarding "Analytical Methods for Detection and Identification" and "Methods of Identification and Analysis" (for details see presentation file). In the discussion Ms Steinborn made it clear that biocides' manufacturers do not have to make appropriate analytical standards available for their compounds. Another question raised was on the availability of measurement uncertainty data for the methods. Ms Steinborn explained that no such data have to be provided.

Bernd M. Gawlik (European Commission, Joint Research Centre) reported on the importance of monitoring in European legislation. He discussed especially the Water Framework Directive which introduced EU-wide harmonised monitoring obligations for priority substances (the list also includes PPP and biocides). One drawback is currently that metadata from sampling and analysis are often not aggregated together with the results data. Mr Gawlik described recent efforts on the development of a pan-European monitoring approach to derive a so-called Watch List of potentially relevant additional substances for monitoring. Thus independent data on the occurrence of less-investigated and new contaminants in environmental media are generated by sharing and synchronising available resources. Another feature of his talk was the description of an approach to share monitoring data EU-wide via an "Integrated Platform for Chemical Monitoring Data" which is intended to help in identifying links between exposure and epidemiological data.

The role of Environmental Specimen Banks (ESBs) in monitoring activities in Europe was described in the contribution of Jan Koschorreck (Umweltbundesamt). He reported that ESBs are operated in several European countries (e.g., in Sweden since the 1960s). ESB investigations can provide evidence for risk management decisions. Data from an ESB monitoring can help to prioritise regulatory action and to verify the success of risk reduction measures (e.g., bans on the use of chemicals of concern). ESBs also allow the identification of contaminants of emerging concern. Mr Koschorreck reported that the different ESBs in Europe mainly host biota samples, thus potentially allowing the analysis of persistent and bioaccumulative substances. An example of biocides covered in ESB investigations are organotin compounds (e.g., in a study of marine biota samples from the German ESB archive; see also poster presented by Knopf et al.). One aspect of the discussion was the possibility of ESB samples provision to third parties. Mr Koschorreck explained that requests for samples from the German ESB could be made to the Umweltbundesamt. Samples may be provided if the study objectives are sound and the data are finally published. Other ESBs have similar policies on sample provision.

Burkhard Knopf (Fraunhofer IME) presented the results from a survey of biocide environmental monitoring activities in Germany which was conducted within a project for the Umweltbundesamt in 2011. The evaluation of returned questionnaires revealed that biocides in particular are covered for surface water monitoring. Mr Knopf reported that the substances covered are mainly those biocides that are also authorised as plant protection products. Examples of compounds which exceeded annual average concentrations of the WFD environmental quality standards (EQS) at some sampling sites in Germany are diuron, lindane, monolinuron and terbutryn. At some sites reported concentrations for triclosan and cybutryne were also above effect concentrations (PNECs). Mr Knopf also mentioned that the survey revealed only a few studies which covered investigations of biocides in sewage treatment plant effluents and sewage sludge, soil or biota samples. One participant was interested in the biocide monitoring data gathered in the study. Mr Knopf responded that aggregated data were gathered and that these are included in a summary table of the study report (e.g., mean concentrations for a period and site, no metadata). The German language report is available from the Umweltbundesamt.

A proposal for the prioritisation of biocides for environmental monitoring was introduced by Heinz Rüdel (Fraunhofer IME). The background for the approach, which was developed in a project funded by the Umweltbundesamt, is the demand for monitoring studies to follow the changes caused by the implementation of the BPD (e.g., effect of phasing-out of certain biocides or substitutions by other compounds on environmental levels of these substances). The proposed concept includes – for each biocide – assessments of emission characteristics, potential effects, and the relevance for their occurrence in important environmental compartments (see also poster presented by Jäger et al.).

The session on “Biocide monitoring in soils, urban environments and biota” was opened with a talk by Burkard T. Watermann (LimnoMar). He reported on a project funded by the Umweltbundesamt which investigates the reliability of exposure prognoses of EU emission scenario models for antifouling biocides in marinas. Mr Watermann presented the development of a comprehensive inventory of leisure boats in marinas and further mooring sites in German coastal and inland waters. Future work will include a screening of water concentrations of antifouling biocides and the comparison of the measured concentrations with those derived from emission models.

Manfred Sengl (Bavarian Environment Agency LfU) presented case studies from the monitoring of selected biocides. He covered results from analysis of triclosan and its metabolite methyltriclosan, cybutryne and biocides which are also used as plant protection products. High levels of cybutryne, for example, were especially found in water samples from yachting harbours at Lake Starnberg (above the proposed EQS of 2.5 ng/L). The long-term monitoring of larger rivers for triclosan revealed slightly decreasing concentrations, while methyltriclosan amounts were constant at a lower level (period 2004-2012). Mr Sengl welcomed proposals for extended biocide monitoring based on a well justified and clearly documented prioritisation process. In the discussion Mr Sengl explained that currently only data for priority substances are reported to the German WFD database operated at the Umweltbundesamt. Some biocide data are thus not included, but some of these additional data have been published in thematic reports.

Harald Rahm (North-Rhine Westphalia State Environment Agency LANUV) reported on the status of biocide monitoring in the German Federal state North-Rhine Westphalia. Biocide monitoring is performed as part of the routine monitoring of surface water and groundwater water (WFD-related) as well as in municipal and industrial wastewaters. Long-term monitoring has made time series available for periods since about 1990 for isoproturon, diuron and terbutryn. Isoproturon, terbutryn and terbutylazine are the biocides mainly detected. Isoproturon and diuron, for example, partly exceeded the WFD EQS. Besides these compounds, tebuconazole was also frequently detected in wastewater. One improvement to be made is the introduction of event-related monitoring to identify maximum concentrations in smaller rivers and brooks. Matrices other than water, e.g., soil, sludge, sediment and suspended particulate matter, are covered in special projects. To inform the public, all LANUV monitoring data are available via an internet portal.

Biocide monitoring activities in Switzerland were presented by Nicole Munz (Swiss Federal Office for the Environment FOEN). A nationwide overview of plant protection products and biocides occurring in streams was compiled for the period 2005-2012. Monitoring is mainly performed by cantonal authorities and focuses on PPP. Of about 300 compounds investigated, 54 were biocides, of which 36 were also authorised as PPP. There were 26 biocides detected at concentrations > 0.1 µg/L (Swiss quality goal for micro-pollutants in surface waters). For compounds which are solely used as biocides, the highest levels were found for N,N-diethylmetatoluamide (DEET; up to 300 µg/L) and propoxur (up to 2 µg/L). Triclosan and Cybutryne were found at levels up to about 0.1 µg/L. Although the highest concentrations of PPP and biocides were found in small and medium water bodies, major sampling activities in Switzerland currently focus on larger streams. In the discussion Ms Munz explained that a value of 0.1 µg/L is used for assessment instead of compound-specific PNECs, because the latter are currently not legally defined.

Alice James-Casas (INERIS) reported on the status of biocide monitoring in freshwaters in France. In recent years a limited number of biocides has been covered in exceptional monitoring campaigns for groundwater and surface water. Out of 22 biocides considered, only four substances were found at levels above the limit of quantification. A watch list of compounds for surface water monitoring in France is currently being compiled. The prioritisation approach is based on the NORMAN scheme and covers ca. 2400 chemicals (industrial chemicals, pharmaceuticals, dual use PPP and biocides, and about 70 biocides without PPP authorisation). About 20 biocides were identified for the watch list, which covers about 240 compounds in total. The monitoring campaign based on this watch list is currently running and will be completed by the end of 2012.

The first speaker in the session "Biocide monitoring in soils, urban environments and biota" was Michael Burkhardt (HSR University of Applied Sciences Rapperswil), who presented the state of knowledge on biocides in façades. He reported that, although a larger number of substances is notified, only about four film preservatives are used in significant quantities. From simulation and field experiments Mr Burkhardt demonstrated a negative correlation between biocide amounts in façade runoff and building height. The biocide release is mainly controlled by water contact time (e.g., dry/wet-cycles accelerate emission). According to Mr Burkhardt, the market has rapidly reacted in recent years to the findings on leaching of biocides from building materials by switching to other compounds or other technologies (e.g., encapsulated biocides). The change to other compounds was confirmed by one participant who reported that certain biocides are no longer available for manufacturers of paints. One participant asked whether a maximum leaching amount for the service life of façade paints could be defined. Mr Burkhardt answered that this seems difficult since the leaching is strongly dependent on weather conditions (e.g., higher on the more rain-exposed façade section of a building).

Irene Wittmer (Eawag) gave a talk on the monitoring of biocides from urban sources compared to agricultural plant protection products. The field study was conducted for one year in a small catchment with mixed urban and agricultural land use in the Swiss Plateau. Sub-catchments with various degrees of urban and agricultural land use were studied along with the outlets of a combined sewer overflow, a separate sewer and a wastewater treatment plant. Ms Wittmer reported that at the beginning of rain events, river discharge consists mostly of urban storm water with biocides, while losses of PPP from agricultural areas were delayed. This could be demonstrated by using appropriate substances as tracer compounds which are only applied as biocide or PPP, respectively. An important finding was that loss rates from the use of urban biocides were partly higher than from agricultural usage of PPP. Apparently the lower usage was compensated by urban loss rates that were significantly higher than agricultural ones.

Jens Jacob (Julius Kühn-Institut) presented preliminary results from an Umweltbundesamt funded project on anticoagulant rodenticides in non-target organisms in Germany. The detected residues in non-target small mammals reflected the baiting campaign with brodifacoum. The highest rodenticide residues were found in individuals (mainly field mice species, bank voles and shrews) trapped close to baiting points. Mr Jacob reported that the data will be used to assess the risk to barn owls from the use of rodenticides on farms.

The three contributions to the final session were intended as an introduction to the topics of the following break-out groups. First Irene Wittmer (Eawag) introduced the Swiss approach on the prioritisation of micro-pollutants for monitoring campaigns. It is intended to identify about 80 compounds for surface water monitoring. About 10 biocides which either have important sources or are ecotoxicologically relevant or are expected in high loads will be included in the selection. From about 380 biocides notified in Switzerland, only 66 compounds were identified as relevant regarding actual usage and stability in water (no inorganic compounds, polymers or quaternary ammonium compounds covered). Rodenticides were not considered, since the usage volume is apparently very low. As prioritisation parameters log K_{OW}, stability in water, and actual biocide usage in products in Switzerland were applied. Relevant compounds were further categorised into those with low ecotoxicological values and those with high. This procedure identified 11 relevant biocides, including four which are only used as biocides (DEET, triclosan, terbutryn, cybutryne). The relevance of further compounds will be evaluated on the base of an analytical screening study in five representative Swiss catchments (e.g., the relevance of the material preservative tebuconazole as a potential micro-pollutant will be investigated). The question was raised why only the water phase was considered and not sediment, too. Ms Wittmer explained that the described prioritisation approach supports the implemented sampling activities in Switzerland which currently cover no sediment sampling.

Arne Wick (German Federal Institute of Hydrology BfG) gave an overview of the analytical challenges for the analysis of biocides in aqueous and solid environmental matrices. Biocides cover a broad compound spectrum with different physico-chemical properties (anionic/cationic compounds, polar/non-polar). Also the relevant matrices – such as wastewater, sludge or sediment – are demanding because of complex constituents. Often a high sensitivity is required because of low effect concentrations. Mr Wick reported from his experiences with a dedicated LC-tandem MS procedure which covers about 45 biocides and/or PPP. Mr Wick recommends the use of labelled surrogate standards (isotope dilution technique) wherever possible, or ionisation by APCI as an alternative. For both procedures relative recoveries for the target compounds were calculated from the recoveries of the analytes by correcting for the recoveries of the surrogate standards. In the discussion Mr Wick reported that the limits of quantitation (LOQs) were estimated from low-level spiked samples. He described that LOQs are calculated for each measurement series since instrument performance at trace concentration levels – and therefore LOQs – may change from day to day.

The contribution by Jaroslav Slobodnik (Environmental Institute, SK) covered monitoring databases and exchange of monitoring data. Mr Slobodnik focused on the experiences of the NORMAN network. For the NORMAN EMPODAT database, data on the occurrence of non-regulated substances in all environmental matrices are systematically collected, the majority of them from aquatic compartments. Currently, more than 1 million database entries on the occurrence of emerging substances from 25 European countries are compiled. These monitoring data are used in the NORMAN prioritisation approach, which results in a list of candidate substances proposed for monitoring in surface waters. The EMPODAT data cover about 350 of the total number of about 700 emerging substances identified by NORMAN, but less than 1% of the data were reported on the occurrence of biocides/PPP. Monitoring data are available for only 22 of the 34 biocides on the NORMAN list of emerging substances. For five of these substances, monitoring data cover more than four countries. For three of these compounds (terbuthylazine, diazinon, terbutryn) a potential risk was identified for the detected environmental levels by the NORMAN assessment. Finally, Mr Slobodnik introduced a further database operated by NORMAN. In the open access MassBank database, mass-spectrometric data on known and unknown compounds detected in water (and other compartments) are stored. The database should support the non-target screening and identification of currently unknown compounds in environmental samples. One participant was interested in the possibility of relating the NORMAN monitoring data to maps. Mr Slobodnik answered that this is not possible, since – because of concerns over confidentiality – the geographical coordinates are not mandatory for the database input.

3 Summary of break-out group discussions

3.1 Summary of break-out group (A) - Prioritisation of biocides for monitoring

Facilitator: Bernd M. Gawlik, Joint Research Centre, Ispra (IT)

Rapporteur: Heinz Rüdel, Fraunhofer IME, Schmallenberg (DE)

This group of about 30 workshop participants discussed as first topic the idea that prioritisation of chemicals for environmental monitoring may be driven by different frameworks. The main background for surface water-related monitoring in Europe so far is the Water Framework Directive (WFD) and additional national regulations. The identification of a substance as a priority substance also has legal consequences since it should not be detected in surface waters above the WFD environmental quality standards (EQS) by 2015. Comparable European regulations with monitoring obligations for other environmental media (e.g., soil) are still not in place. In the context of biocide risk assessment (and also for other regulations, e.g., REACh) an environmental monitoring activity may have another purpose, too: here it may be required to prove the success of the regulations by trend monitoring. For example, it may be investigated whether environmental concentrations of those biocides that will not be marketed under the Biocide Products Directive (BPD) and the follow-up regulation 528/2012 will be decreasing after the non-inclusion decision is fully implemented. Another aspect could be the identification of possible substitute compounds for biocides that are no longer supported. For the substitutes, environmental concentrations may rise because of increased market demands. A third aspect may be the surveillance of biocides for which risk mitigation measures were implemented in order to verify their success (refer to the workshop presentation by Nöh et al.). Another reason for monitoring could be the need for measurement data for the development and validation of exposure models. Although post-authorisation monitoring is currently not implemented in the BPD or the follow-up regulation (EU regulation 528/2012), such measures would allow it to be proved that the use of biocides is safe and would enable the detection of possible changes induced by the European biocide regulations.

Generally, the prioritisation of relevant compounds for environmental monitoring is a systematic approach. In the past, monitoring efforts were partly concentrated on well-known pollutants while new compounds were not addressed because no occurrence data were available (see also workshop contributions by Dulio & Slobodnik and Gawlik). Prioritisation could put new compounds on the radar and identify those which are no longer of interest.

It was also highlighted that a prioritisation approach should consider all relevant compounds. There should be no ruling-out of possibly relevant compounds, e.g., by the fact that currently no appropriate analytical methods are established. However, data which are urgently needed for prioritisation have not yet been available for all biocides, as the majority of substances are still under review. The Umweltbundesamt is currently working on collecting at least temporary data from the corresponding reporting member states.

From the different aspects to be considered there was agreement that consumption figures for biocidal substances are very important. Unfortunately these data are not readily available. Authorisation agencies may have confidential data for production/ consumption volumes of biocides, but the biocides market is much more diversified than the pesticides market. For pesticides, the market seems more transparent, since registrations are held mainly by large companies. For biocides, on the other hand, a large number of smaller companies is placing products on the market (up to several thousand products with one biocidal active ingredient) and the application areas are much broader as compared to pesticides (large number of product types). It was discussed that in future the "letter of access" procedure may be used to generate consumption volumes: for Annex I biocidal compounds, data owners may grant other manufacturers access to data. During this step an intended production volume could be documented.

It was also discussed which environmental media and compartments are of relevance for biocide monitoring. The workshop presentations were dominated by examples from surface water monitoring (mainly water phase, in some cases sediments or suspended particulate matter; e.g., Sengl et al., Rahm & Vietoris, Munz et al.). However, some contributions also covered terrestrial compartment monitoring (rodenticides in non-target organisms; see oral contribution by Broll et al. and poster presented by Buckle & Prescott).

Especially for those biocides that have persistent and bioaccumulative (PB) properties, biota monitoring could provide useful information on possible long-term effects. In this context appropriate samples archived in environmental specimen banks (ESBs) could be used. ESBs usually cover time series samples from selected sites and allow retrospective trend monitoring (see workshop contribution by Koschorreck and posters by Rüdel et al. and Knopf et al.).

The further discussion covered other possible information which could be used for the prioritisation process. One suggestion was to use the information from the biocide product type (PT) as surrogate for exposure relevance. The PT could give a hint as to which compartment may be most relevant for the monitoring of the respective biocide (e.g., as shown in the workshop contributions by Broll et al. and Buckle & Allan, rodenticides monitoring may be most relevant in biota samples from the terrestrial environment). A more detailed evaluation of the environmental exposures of biocides from different PT was performed in a study for the EU Commission (COWI A/S, Kongens Lyngby, DK, 2009; see also oral contribution by Rüdel et al.).

Agreement was achieved on the statement that each prioritisation approach should be complemented by screening investigations. The analytical data gained should help to assess the plausibility of the prioritisation scheme and to verify that no relevant substance is lost. In this context it was suggested to include sewage treatment plants (STP) in biocide monitoring. Since a major part of biocides from products used in urban areas or households is disposed of in wastewater, effluents of STP and sewage sludge potentially contain residues of biocides (see also presentations by Wick et al. and Rahm & Vietoris). Monitoring these matrices could give valuable information on biocides entering the aquatic or terrestrial environment. The data could also be used to further validate simulation models which are applied to estimate the distribution of biocides in an STP and to assess the elimination potential of STPs (see workshop contribution by Nöh et al.).

A participant commented that the development of a list of "substances for monitoring" by a prioritisation approach could have an effect on future usage of the affected biocides. An example was given from Switzerland, where Cybutryne is no longer used in façade protection and antifouling products as a consequence of discussions on the environmental relevance of the compound. Owing to increased customer awareness, companies tend to avoid substances that are seen as a potential problem. A consequence of this possible effect is that a priority list of biocides for monitoring should be reviewed regularly, since changes in the market could occur rapidly.

A further topic of the discussion was the suggestion to bring the presented prioritisation approaches (NORMAN, CH, DE) together. All schemes have similar components, e.g., use of substance properties for assessing the relevance of a substance for a certain compartment, ecotoxicity data for assessing the relevance of environmental effects, use of substance properties-based assumptions on exposure pathways and potential inputs into the environment. However, since the prioritisation approaches have different objectives, differences may remain. It was suggested that further discussion on this topic should be organised in the framework of NORMAN.

Finally the workshop participants concluded that each prioritisation approach should be transparent and clearly communicated. Ideally it should also involve all stakeholders (e.g., assessment authorities, national/regional monitoring institutions, manufacturers and distributors, consumer organisations). It was also discussed who should pay for the environmental monitoring of biocides (society vs. manufacturers/users), although no answer was found to this question.

3.2 Summary of break-out group (B) - Practical aspects of sampling and analysis

Facilitator: Peter Lepom, Umweltbundesamt (DE)

Rapporteur: Jan Schwarzbauer, RWTH Aachen (DE)

This discussion group consisted of approximately 15 persons. As an introduction Peter Lepom set out the framework of this break-out group. Suggested aspects covered *inter alia* the general objective of biocide monitoring, analytical problems, matrix-related problems and quality of data.

The discussion started with the question on the general objectives and the overall aim of biocide monitoring. Generally, two different types of monitoring programmes have been identified, (i) general monitoring programmes, which are performed continuously and (ii) specific monitoring programmes, which are initiated temporarily. Later ones are appropriate for more specialised questions, e.g., the verification of emission scenarios, the differentiation of emission sources, or the characterisation of primary contamination. But it became obvious that different types of monitoring programmes need different monitoring strategies, including parameters such as number and location of sampling sites, spectra of compound or sampling frequency.

Thereafter, more general problems of biocide monitoring were discussed. The lack of comparability between different data sets and the restricted availability of metadata and background information were then noted. This hindrance affects the assessment of obtained data and values. Lastly, with respect to monitoring programmes, current interests and needs have to be harmonised in particular for fruitful cooperation between industry and authorities.

The discussion then moved on from these general points to more specific aspects. To optimise monitoring measures, a properly focused choice needs to be made of sampling locations, sample material and sampling frequency. With respect to data handling, the most important aspect is to provide appropriate sampling information (e.g., composite or spot sample, frequency etc.), in general, a suitable metadata set.

The discussion then turned to the analytical aspects. In particular, several analytical requirements for suitable monitoring were identified. All participants agreed that the measurement of blank values has to be a substantial part of monitoring analyses and characterises the quality of monitoring results. The limit of quantitation (LOQ) was discussed as a second very sensitive parameter. Fitting LOQs with the environmental requirements seemed to be the best strategy. LOQs should therefore be orientated towards EQS or PNEC of the respective biocides. The main limiting factor associated to the application of multi-residue methods is in general represented by a reduced analytical performance of these techniques in terms of “low LOQs”. In fact, there is a trade-off between high throughput and high sensitivity which needs to be taken into account. As a last important analytical requirement the consideration of measurement uncertainty in monitoring reports was called for, in particular for suitable data interpretation (e.g., for time trend studies).

Two further specific analytical aspects were related to analytical methods. Firstly, the lack of labelled standards for many relevant biocides was identified as a major hindrance. It often reduces the accuracy of measurements and, consequently, of the overall monitoring dataset. The group came up with one suggestion: after prioritisation the availability of labelled substances for the most important candidates should be checked, and – for missing reference compounds – joint acquisition by *de novo* synthesis should be initiated. Here NORMAN could possibly serve as forum. Secondly, the discussion clearly pointed to the necessity of the complementary usage of GC/MS and LC/MS protocols, since there exists no general method applicable for all biocides and, consequently, for a comprehensive monitoring measure.

Finally, the break-out group focused on matrix aspects. After a short discussion all participants agreed with the following important conclusions: (i) biocides' properties and environmental fate are the major factors in determining the compartment where they should be analysed and (ii) water is important, but not the only relevant matrix.

At this point the break-out group finished their very fruitful and constructive discussion and ended up with one very important, overarching statement:
The first monitoring activity: define the question the monitoring programme is intended to answer!

3.3 Summary of break-out group (C) - Databases and exchange of monitoring data

Facilitator: Gerlinde Knetsch, Umweltbundesamt (DE)

Rapporteur: Jaroslav Slobodnik, Environmental Institute (SK)

One of the objectives of the workshop was to establish a platform for (i) exchange of existing information and data on exposure pathways for biocides, and (ii) monitoring data handling and evaluation. Experts interested in these topics met in this break-out group. The discussion was focused on four major areas (cf. below) and recommendations for follow-up actions were then presented for critical review and comments of other workshop participants at the plenary session.

Quality and comparability of the data on biocides:

There was unanimous agreement on the urgent need to improve quality of data. A widespread practice of reporting monitoring data on biocides with analytical methods having a limit of quantification (LOQ) higher than the predicted no effect concentration (PNEC) value often gives a misleading impression about the actual occurrence of biocides in the environment. A recommendation was made to make it obligatory to report LOQs and limits of detection (LODs) and to compile available LOQs from different laboratories in order to identify needs for improvement of analytical methodologies. NORMAN Method Validation Protocols and standard operating procedures (SOPs) developed, e.g., by the German Environmental Specimen Bank were proposed as a starting point for the assessment of the analytical methods used.

It was concluded that there is a need for improved data comparability at the EU scale, and a recommendation was made to harmonise data collection formats using the existing NORMAN Data Collection Templates as a reference.

Databases:

The need for a central European biocide database was stressed. A pragmatic proposal was made to use the existing web-based NORMAN database, but with a strong suggestion that it should be extended to include a full list of biocides. An alternative option of creating a new dedicated biocides database using the same data collection formats as the NORMAN database was considered. Examples of other existing databases (IUCLID, Pesticide Atlas (NL), UBA, NRW, Baden-Wuerttemberg (DE)) were proposed to be studied before the final decision.

Independently of the above, the development of a long list of biocides was proposed, with reference to their classification under various regulatory frameworks. Considering the frequent overlaps in the definition of a "biocide", substances used exclusively as biocides should be specifically flagged (coded) in the database(s).

It was also agreed that data on rodenticides in animals should be included in the database(s).

Various stakeholders, including industry, expressed interest in finding a one-stop-shop for all (mainly monitoring) data on biocides. A proposal was made to equip the biocide database with links to all other databases dealing with biocides.

Special care should be taken to develop the database towards “Service Oriented Architecture” (OECD recommendation). All new databases should be established in a Java/web-based version ensuring their eventual interlinking.

A strong need was identified to collect information on the use pattern/usage of biocides in order to be able to predict future pollution. A proposal was made to start with available usage data (e.g. in Nordic countries). It was agreed that this activity would require closer cooperation with industries.

Communication of the data:

There were several opinions on the accessibility of data, but the prevailing one was to keep access to raw data open to anyone and access to pre-processed/aggregated data open to selected users/interest groups. A counter-proposal suggested sharing pre-processed data with the public and restricting access (at several user levels) to the raw data. It was proposed that the message to be addressed to the public should simply answer the question: “What is the state of our environment?“. It was also mentioned that designing a proper level of aggregation might be difficult and could prevent correct decision-making.

Participants agreed that a special effort should be made to establish trust in the data and that the database should therefore contain as much information as possible (even if in a coded form) and users should be directed to pre-designed “Frequently Asked Questions”.

Data sharing/exchange:

First steps towards the creation of the central EU biocide database were made by receiving commitment by workshop participants to provide data presented at the workshop to the NORMAN database. All participants were asked to check if and when this is possible. In Germany, a template for data collection is planned to be developed by March 2013 and then a data collection/sharing campaign will start.

4 Workshop closing remarks

Stefanie Jäger (Umweltbundesamt, UBA) summarised the results of this workshop. UBA was very happy to have had the opportunity to host this first workshop on biocide monitoring. Important questions and obstacles were presented and discussed in the workshop. The participants learned about needs and data gaps on the one side and about existing data and prioritisation efforts on the other. The results had to be understood as a first step toward integrating the topic of biocide monitoring in the monitoring community. UBA was sure to use the outcome of the workshop for an UBA research project on biocide monitoring which had recently started and hoped that the participants could also take home some new ideas.

UBA hoped that from now on the exchange of experiences on biocide monitoring at EU level and national level would improve. In the current research project, UBA was planning to maintain close contact with NORMAN as well as with the German federal state authorities – to share experiences, data and ideas.

Ingrid Nöh (Umweltbundesamt) closed the workshop after thanking all participants for coming, for their contributions and for the fruitful discussions. She announced a second workshop on biocide monitoring which will take place in 2015 when the UBA research project will be finished and invited all participants to attend.

5 Workshop programme

5.1 Day 1

Welcome address

Petra Greiner, Umweltbundesamt, Dessau-Rosslau (DE)

Introduction

Chair: Petra Greiner, Umweltbundesamt, Dessau-Rosslau (DE)

Why is a biocide monitoring necessary? Introduction of the regulatory background
Ingrid Nöh, Stefanie Jäger, Silke Müller-Knoche, Umweltbundesamt, Dessau-Rosslau (DE)

The NORMAN network - Gathering information on occurrence and environmental effects of emerging substances
Valeria Dulio, NORMAN, Verneuil-en-Halatte (FR), Jaroslav Slobodnik, Environmental Institute, Kos (SK)

Session I – General aspects of (biocide) monitoring

Chair: Petra Greiner, Umweltbundesamt, Dessau-Rosslau (DE)

Analytical Methods for monitoring of biocides in the environment - are the data requirements sufficient?

Angelika Steinborn, Lutz Alder, Federal Institute for Risk Assessment (BfR), Berlin (DE)

(Biocide) monitoring in European legislation - The WFD example
Bernd M. Gawlik, European Commission, Joint Research Centre, Ispra (IT)

European Environmental Specimen Banks
Jan Koschorreck, Umweltbundesamt, Berlin (DE)

Survey of biocide environmental monitoring data in Germany
Burkhard Knopf, Fraunhofer IME, Schmallenberg (DE), Stefanie Jäger, Stefanie Wieck, Silke Müller-Knoche, Ingrid Nöh, Umweltbundesamt, Dessau-Rosslau (DE)

Proposal for the prioritisation of biocides for environmental monitoring
Heinz Rüdel, Fraunhofer IME, Schmallenberg (DE), Stefanie Jäger, Stefanie Wieck, Silke Müller-Knoche, Ingrid Nöh, Umweltbundesamt, Dessau-Rosslau (DE)

Session II – biocide monitoring in surface waters

Chair: Petra Greiner, Umweltbundesamt, Dessau-Rosslau (DE)

Antifouling biocides in German coastal and inland waters - How reliable are exposure prognoses of EU emission scenario models for marinas?
Burkard T. Watermann, LimnoMar, Hamburg (DE), Michael Feibicke Umweltbundesamt, Berlin-Marienfelde (DE)

Monitoring of selected biocides - experiences from Bavaria
Manfred Sengl, Siegfried Frey, Katharina Späth, Bavarian Environment Agency (LfU), Munich (DE)

Status of biocide monitoring in North-Rhine Westphalia, Germany
Harald Rahm, Friederike Vietoris, North-Rhine-Westphalia State Environment Agency LANUV, Düsseldorf (DE)

Biocide monitoring in Switzerland
Nicole Munz, Christian Leu, Federal Office for the Environment (FOEN), Bern (CH),
Irene Wittmer, Eawag, Dübendorf (CH)

Status of biocide monitoring in France
Alice James-Casas, Valeria Dulio, Sandrine Andres, INERIS, Verneuil-en-Halatte (FR)

Session III – Biocide monitoring in soils, urban environments and biota

Chair: Ingrid Nöh, Umweltbundesamt, Dessau-Rosslau (DE)

Biocides in facades - State of knowledge
Michael Burkhardt, Conrad Dietschweiler, HSR University of Applied Sciences, Rapperswil (CH),
T. Wangler, ETH Zürich Institute for Technology in Architecture, Zurich (CH)

Monitoring of biocides from urban sources compared to agricultural plant protection products
Irene Wittmer, H.-P. Bader, R. Scheidegger, H. Singer, C. Stamm, Eawag, Dübendorf (CH)

Anticoagulant rodenticides in non-target biota in Germany: residues in non-target small mammals
Anke Broll, Jens Jacob, Alexandra Esther, Detlef Schenke, Julius Kühn-Institut, Münster (DE),
Erik Schmolz, Umweltbundesamt, Berlin (DE)

General discussion and summary of day 1

5.2 Day 2

Session IV – Introduction to break-out groups

Chair: Valeria Dulio, NORMAN, Verneuil-en-Halatte (FR)

Prioritisation of biocides for monitoring campaigns in Switzerland
Irene K. Wittmer, C. Moschet, H. Singer, C. Stamm, Eawag, Dübendorf (CH), M. Junghans, Ökotoxzentrum, Dübendorf (CH), Christian Leu, Nicole Munz, Federal Office for the Environment (FOEN), Bern (CH)

Analytical challenges for the analysis of biocides in aqueous and solid environmental matrices
Arne Wick, Kathrin Broeder, Michael Schluesener, Thomas Ternes, German Federal Institute of Hydrology BfG, Koblenz (DE)

Databases and exchange of monitoring data - experiences from NORMAN
Jaroslav Slobodnik, Environmental Institute, Kos (SK)

Parallel break-out groups

(A) Prioritisation of biocides for monitoring // facilitator/rapporteur: Bernd M. Gawlik, European Commission, Joint Research Centre, Ispra (IT), and Heinz Rüdel, Fraunhofer IME, Schmallenberg (DE)

(B) Practical aspects of sampling and analysis // facilitator/rapporteur: Peter Lepom, Umweltbundesamt, Berlin (DE), and Jan Schwarzbauer, GGCP RWTH, Aachen (DE)

(C) Databases and exchange of monitoring data // facilitator/rapporteur: Gerlinde Knetsch, Umweltbundesamt, Dessau-Rosslau (DE), and Jaroslav Slobodnik, Environmental Institute, Kos (SK)

Reports from break-out groups in the plenary and discussion
Chairs: Heinz Rüdel, Fraunhofer IME, Schmallenberg (DE),
Stefanie Jäger, Umweltbundesamt, Dessau-Rosslau (DE)

Conclusions and closure of the workshop
Stefanie Jäger, Ingrid Nöh, Umweltbundesamt, Dessau-Rosslau (DE)

5.3 Poster

1. Preparation of a prioritisation concept for the monitoring of biocides – Refinement of the data set used for the regulation of biocides // Stefanie Jäger et al.
2. Verification of the success of recent use restrictions for tributyltin by retrospective monitoring of archived biota samples from North and Baltic Sea // Burkhard Knopf et al.
3. Retrospective monitoring of methyltriclosan in freshwater fish covering the period 1992-2008 // Heinz Rüdel et al.
4. Triclosan and Methyltriclosan in suspended particulate matter - Results from the German Environmental Specimen Bank // Mathias Ricking et al.
5. Long-term monitoring of second-generation anticoagulant rodenticides in non-target wildlife in the UK // Richard F. Shore et al.
6. Monitoring Impacts of Vertebrate Pesticides in the UK: 1993 to 2011 // Alan Buckle and Colin Prescott
7. Non-target screening analyses of organic contaminants in river systems as a base for monitoring measures // Jan Schwarzbauer and Mathias Ricking
8. The use of experimental data to estimate long term biocide leaching ratios from wooden facades // Morten Klamer
9. Dynamics of biocide emissions from buildings in a suburban stormwater catchment // Ulla E. Bollmann et al.
10. Emission Scenario Documents (ESD) for biocidal products: Data refinement via questionnaires // Nathalie Costa Pinheiro et al.
11. Antifouling-Wirkstoffe in deutschen Sportbootrevieren - Wie verlässlich lassen sich Einträge vorhersagen? // Burkard T. Watermann et al.

6 Abstracts – oral presentations

6.1 Why is a biocide monitoring necessary? – Introduction of the regulatory background

Ingrid Nöh, Stefanie Jäger, Silke Müller-Knoche*

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Due to the entry in force of the EU Biocidal Product Directive (BPD) 98/8/EC in 1998, use of active substances changed. Decisions on the approval of active substances in the Annex I of the directive and product authorisations lead to changed uses. Furthermore, changes can be expected for production and application volumes, emission quantities as well as in the application pattern of biocides. Monitoring data can be one tool to ensure a realistic estimation of the environmental exposure by biocides which is a prerequisite for an effective and realistic environmental risk assessment in biocide regulation and a possible proof of effectiveness of risk mitigation measures (RMM). A literature study performed by UBA in 2009 as well as a research project of Fraunhofer IME, funded by UBA in 2011, have shown that the amount and nature of available monitoring data are currently insufficient for biocidal substances. As a consequence of the European Water Framework Directive (2000/60/EC), countries are obliged to collect monitoring data in surface waters for several substances in order to reach and survey the defined Environmental Quality Standards (EQS, 2008/105/EC). Some of those active substances are simultaneously used in biocidal products as well as in plant protection products (PPP), pharmaceuticals and/or chemicals. When a substance is not exclusively used in biocidal products, it is often not possible to decide whether the source is a biocidal one or a result of entries from pharmaceuticals or plant protection products.

However, as the authorisation of biocidal products has just started, it is now the last opportunity to generate a baseline of the initial exposure situation and subsequently to observe changes of biocide emissions into the environment as consequence of the authorisation. The changes in environmental exposure to biocides can be related to expiring marketing authorisation, e.g. when biocides are not included in Annex I of BPD. On the other hand, it might be possible that environmental concentrations of some substances increase when those substances are used as substitutes for other substances which have lost or will lose their marketing authorisation. Declining exposure trends can also result from efficient risk mitigation measures as an additional requirement of product authorisation.

This presentation intends to give a short overview of the regulatory background, the needs for environmental monitoring data and the possibilities to use available monitoring data on the way forward to a realistic environmental risk assessment of biocides, e.g. to refine risk mitigation measures or improve exposure scenarios.

6.2 The NORMAN network - Gathering information on occurrence and environmental effects of emerging substances

*Valeria Dulio*1, Jaroslav Slobodnik2*

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The NORMAN network (www.norman-network.net) is an independent forum of more than 50 reference laboratories, research centres and related organisations which disseminates information on emerging environmental substances and seeks to harmonise methods for measurement of their level of occurrence in the environment and effects on ecosystems. The final aim is to help the identification and prioritisation of relevant emerging contaminants responsible for observed adverse effects on ecosystems and human health.

This presentation focuses on some key activities performed by the network to achieve this objective. A list of 706 "emerging substances" frequently discussed in the scientific literature (of which 163 identified as pesticides or biocides) was compiled in 2010 and is regularly updated by the NORMAN experts. This list represents the main input for the prioritisation work carried out by NORMAN using a scheme specifically designed for emerging substances (i.e. substances for which knowledge gaps are identified and actions needed at either the research or management level).

In support of the NORMAN activities and of this prioritisation work, since its creation, NORMAN has been maintaining and regularly feeding three publicly available web-based databases. Among these, EMPODAT collects available geo-referenced monitoring data and ecotoxicological information from bioassays from leading research institutions in Europe and beyond. At the end of 2011 EMPODAT contained more than 1 million entries on the occurrence of emerging substances from 25 European countries in water, sediment, biota and air matrices. Out of the 706 substances identified by NORMAN, 359 were supported with occurrence data (collected in the same formats used by DG ENV for the collection of monitoring data at the EU level for the review of the list of WFD Priority Substances). In addition, information on the ecotoxicity thresholds (lowest PNEC values, measured and/or predicted by Read-Across QSAR modelling) and expected distribution in air/water/soil matrices (via fugacity modelling) was collected for all of the substances. The analytical performance of European laboratories could be judged for more than 400 substances from both the Limits of Quantification (LOQs) of the analytical methods provided with the data and LOQs extracted from the literature.

All these data allow for critical evaluation and prioritisation of emerging substances both at a national level and in a wider international context.

6.3 Analytical methods for monitoring of biocides in the environment – are the data requirements sufficient?

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The European Biocidal Product Directive 98/8/EG (BPD) and the Regulation (EU) No 528/2012, which shall apply from 01/09/2013 established criteria for the placing of biocidal products on the market. Some of these criteria refer to analytical methods to detect relevant residues of biocides in environmental matrices, in body fluids and tissues. These methods are intended for monitoring purposes in relevant environmental media, for identification of misuse and for control of compliance with established limit values. In addition, residue analytical methods for food and feeding stuff may be required for biocidal products which come into contact with food and feeding stuffs. They are necessary for the control of compliance with MRLs and the generation of data for dietary risk assessment.

Due to the diversity of product types and fields of application of biocidal products the above mentioned legal acts include some 'case by case' data requirements and offer the waiving of individual obligations. The regulatory authorities have to decide on waiving arguments and to define the analytes, action values (limit of quantification) and matrices for method validation depending on chemical, toxicological and ecotoxicological properties of the active substance. Generally, for soil, drinking water, surface water and air residue analytical methods should be submitted. From previous evaluations of active substances it became obvious that clear rules for waiving of matrices and for consideration of additional compartments are currently missing.

A further important point is the decision, which compounds form the relevant residue of a biocidal product in a certain matrix, because for those analytes validated methods are required. Unfortunately, such residue definitions are rarely discussed and sometimes even not mentioned in evaluation reports. In the case of active substances which represent multi-component mixtures or biocides with variable composition a definition of (eco)-toxicologically relevant marker substances is necessary.

The main validation data to be provided are defined in the Addendum for the Technical Notes for Guidance (TNsG) on Data Requirements. The required extent of validation is often comparable to the procedure for authorisation of plant protection products, but the guideline for the validation of pesticide residue methods is more up to date with respect to available analytical techniques and the validation extent for confirmatory methods.

6.4 (Biocide) monitoring in European legislation - The WFD example

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Human consumption, irrigation, environmental requirements, recreational needs, cost, energy consumption and pollution all have an impact on the availability and quality of water. The use of biocides and their occurrence in the environment are only reflecting these competing water demands among some of the related economic sectors.

Research has shown how rapidly new substances end up in wastewater, rivers and groundwater, even in drinking water. The knowledge regarding the underlying processes is essential to support proper technological solutions, a market of growing importance also for Europe. To contribute to the innovation in this field, scientific sound references and indicators supporting regulatory and technological innovation in the field of water pollution and its control are needed. Last but not least, a growing and critical public perception towards chemicals ask for more independent and transparent information about occurrence, levels and risks associated to the use of substances such as biocides. Similarly, the understanding and knowledge what chemical pollutants are relevant and how to accurately quantify their concentration continuous to be pivotal to properly assess the chemical status of water bodies.

The generated chemical monitoring information, obtained from monitoring obligations set by EU-legislation, is the here assuming a key role for water governance. This information becomes the more precious the less a pollutant has been investigated and the need to make best use of this information by facilitating access to it is obvious. In this setting, the Water Framework Directive plays a key role in identifying priority substances, establishing environmental quality standards and giving guidance how to monitor.

Being the European Commission’s in-house science service, the Joint Research Centre interacts directly with stakeholders in the Commission and Eco-Industries to promote the necessary regulatory innovation. Improved access to chemical monitoring information generated for the assessment of aquatic environments and a better database in support to new Environmental Quality Standards are a key priority of the JRC.

The talk presents recent developments on the development of an experimental and pan-European monitoring approach in support to a so-called Watch List of potentially relevant substances, as well as the approach to better share chemical monitoring data stemming from various sectorial policies of EU via an Integrated Platform for Chemical Monitoring Data.

6.5 European Environmental Specimen Banks

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What are environmental specimen banks?

An environmental specimen bank (ESB) is an archive for samples that can be used to document and assess the quality of the environment in which we live. These samples are used as eco-toxicological and toxicological evidence for chemical risk management. They samples enable retrospective analyses of substances that were not yet known, or could not be analysed, or were not considered to be important, at the time of sampling.

How do environmental specimen banks work?

Depending on the design of the environmental specimen bank concept, a selection of environmental and human specimens is collected at regular intervals. These specimens are then preserved in such a way that they can still be analysed years and decades after they were collected. It is basically extremely low storing temperatures that that rule out any long-term alteration of the biological and chemical information within the sample.

How do environmental specimen banks support chemical regulation?

Environmental specimen bank investigations can help to prioritise regulatory and industry action. In the latter case chemical risk management can use environmental specimen bank data as toxicological and ecotoxicological evidence to justify additional data requirements or risk reduction measures, e.g. marketing restrictions or even a total ban for the use of the chemical of concern.

What kinds of samples are stored in environmental specimen banks?

The specimens are collected in typical ecosystems all over Europe, including coastal regions, rivers and streams, urban settlements and mountainous terrain. Take the marine environment as an example, where specimens from a range of species are sampled and archived, e.g. from algae, mussels, various fish species, bird eggs and even marine mammals. Some of the larger environmental specimen banks also collect specimens from human populations, including milk, blood and urine from volunteers.

What environmental specimen banks are there in Europe?

Environmental specimen banking actually started in Europe. The oldest environmental specimen bank is located in Stockholm, Sweden and dates back to the 1960s. Today, there is a large diversity of specimen banks across Europe: Environmental specimen banks are in central Europe (Germany, The Netherlands, United Kingdom), Southern Europe (Italy, France, Spain, Portugal) and Northern Europe (Sweden, Denmark/Greenland, Finland, Norway).

What chemicals are analysed?

Environmental specimen banks are traditionally tied to industrial chemicals that are persistent and bioaccumulative, e.g. legacy POPs and PBT substances. Recently, also polar substances have been analysed including substances that are used as personal care products or pharmaceuticals. Organotin compounds are meaningful examples of biocides.

6.6 Survey of biocide environmental monitoring data in Germany

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The German Federal Environmental Agency intends to develop a concept for a future environmental monitoring of biocides in Germany. After implementation the monitoring should allow an investigation whether the taken environmental protection measures caused by the implementation of the European Biocidal Products Directive (BPD, 98/8/EC), which was transposed into German law in the year 2002, had an impact on potential environmental burdens of biocides.

To assess the current status an overview of activities in the field of environmental monitoring of biocides was gained. Therefore, institutions that operate monitoring programmes (e.g., authorities in the German federal states) as well as working groups at universities, which potentially carry out monitoring projects, were contacted and requested to answer a questionnaire. In total about 80 questionnaires were sent out.

About 25 of the contacted persons/institutions responded and provided partly comprehensive reports. The evaluation of the responses revealed that biocides in particular are covered for surface water monitoring. This is mainly caused by provisions of the Water Framework Directive (WFD) and the German Surface Water Ordinance (OGewV), in whose parameter lists also biocidal substances are contained. However, predominantly the covered biocides are those that are also authorised as plant protection products (or at least until recently were). In some of the federal states a similar set of biocides investigated in surface waters is also covered in ground waters. Only a few federal states reported results from investigations of biocides in sewage treatment plant effluents and sewage sludge, or in soil.

Acknowledgement: The authors thank all persons/institutions which responded to the questionnaire and supported the elaboration of this survey report.

6.7 Proposal for the prioritisation of biocides for environmental monitoring

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The European Biocidal Product Directive (BPD, 98/8/EC) causes a change of the use of biocidal active substances in EU member states. This hypothesis may be proven by an environmental monitoring. Therefore, a project was initiated by the German Federal Environment Agency to develop a concept for the selection of biocides for such a monitoring (FKZ 360 04 036).

An important aspect for the prioritisation of substances for a monitoring is the knowledge on the entry pathways of the target compounds into the environment. In Germany, up to now only few data on this topic are available. As pragmatic approach, a study on the environmental relevance of biocides, which was conducted on behalf of the European Commission (COWI 2009), was evaluated to gain information on direct and indirect entry pathways of biocides into environmental media. On basis of this information and based on the results from a biocide monitoring survey and a literature search relevant environmental compartments were identified in which a monitoring should take place.

The proposed concept for the prioritisation of biocidal substances for an environmental monitoring consists of three steps. In a first step compounds are evaluated for emission characteristics (mainly based on intended use in BPD product types). The second step covers potential effects. The scores from both steps are combined and used to prioritise compounds. In a third step it is evaluated in which environmental compartment a compound should be investigated (e.g., water, sediment, biota, soil). This evaluation is based on use patterns (product type specific emissions) and substance specific properties relevant for the compartment regarded (e.g., partition between compartments, persistence or BCF). The procedure was tested with a set of 80 biocides which are either already authorised biocides (BPD Annex I) or candidates (biocidal substances currently in the BPD review programme). The required data were retrieved from assessment reports for biocidal active substances (partly confidential so-called Doc I-reports) or from literature sources.

Finally, the plausibility of the prioritisation is discussed with regard to the compiled monitoring data as well as to prioritisation results from other studies.

6.8 Antifouling biocides in German coastal & inland waters - How reliable are exposure prognoses of EU scenario models for marinas?

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Numerous laboratory and mesocosm studies have demonstrated effect levels of selected antifouling biocides in some regions to have reached critical levels and further findings point at high persistence for some of these chemicals. A prerequisite for robust calculations of environmental antifouling concentrations released from leisure boats is a reliable inventory of boats and the regional distribution of marinas and further mooring sites. For Germany, such area wide data are lacking so far. On this background, a comprehensive survey has been initiated, funded by the Federal Environment Agency (UFOPLAN 2011, FKZ 3711 67 432) in order to quantify the amount of leisure boats in marinas and other locations in inland and coastal waters. Additional local data such as the extension and area of the water body, number of boats at berth during the sailing season, characteristics of adjacent water bodies of the marina were also monitored. Based on these data, local and regional hot spots will be identified and statistically evaluated. In a second work package, water concentrations of antifouling biocides currently in use will be screened in 50 selected marinas in order to demonstrate the variety found in German leisure boat harbors. Finally, these measured concentrations will be compared with those calculated from emission scenarios like MAMPEC and REMA for selected marinas. A statistical evaluation of all data will be performed in order to test the suitability of emission scenarios for German leisure boat areas with high density and multiple use.

6.9 Monitoring of selected biocides – experiences from Bavaria

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Although there is no systematic approach for monitoring biocides in Bavaria a certain amount of data is available for selected biocides as triclosan and its metabolite triclosan-methyl, cybutryne and biocides also used as pesticides. These data were mostly generated for surveillance monitoring according to the Water Framework Directive, for long-term regional monitoring programmes or to fulfil the requirements of the former Directive 76/464/EC.

The anti-fouling agent cybutryne analysed in 6 large rivers monthly for one year showed maximum concentrations of 1.5 ng/L. The annual averages are well below the proposed environmental quality standard (EQS) for inland waters of 2.5 ng/L. These results were confirmed in 2012 by analysing 8 smaller rivers showing a maximum cybutryne concentration of 1.3 ng/L. In closed yachting harbours at Lake Starnberg water concentrations up to 10 ng/L were detected.

A long-term monitoring of larger rivers for triclosan and triclosan-methyl (2004-2012, 2 samples per year) shows slightly decreasing concentrations for triclosan (maximum 20 ng/L in river Regnitz). Triclosan-methyl is accumulating in suspended solids (average 9 µg/kg dw) and biota (wild fish, average 6.1 µg/kg fw, different species, 2003, n=55; mussels, average 6.9 µg/kg fw). Carps from bioaccumulation ponds run with purified waste water show even higher concentrations (average 22 µg/kg fw) of triclosan-methyl after 6 months of exposition.

Pesticides data are available from many monitoring programmes during the last 25 years. 81 biocides are or were also used as pesticides in Germany (status as of 2010, see Fraunhofer IME 2012). 21 out of these substances are monitored in smaller rivers on a regular basis showing significant concentrations e.g. for isoproturon, diuron or terbutryn. For terbutryn, which lost the authorisation as a pesticide in 2002, in total 1336 positive results (8438 data entries from 1998-2010) are listed for surface waters. The maximum concentration of 106 µg/L came from the run-off of a biocide-treated flat roof into a small creek.

Up to now biocide analysis was more or less a by-product of common monitoring activities. So a proposal for biocide monitoring based on a clearly documented prioritisation process is really welcome to fill the data gaps.

6.10 Status of biocide monitoring in North-Rhine Westphalia, Germany

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North-Rhine Westfalia (NRW) performs a large scale environment monitoring that includes biocide monitoring as well as many other aspects. To report biocide monitoring in NRW means to have a look at the monitoring activities of LANUV NRW, the superior state authority of the Ministry for Climate Change, Environment, Agriculture, Conservation of Nature and Consumer Protection.

Biocides are monitored

- in the river Rhine and important tributaries in average samples up to three times daily,
- in WFD surface water monitoring in 4-13 samples a year in peculiar water bodies,
- in WFD groundwater water monitoring regularly in peculiar water bodies,
- in municipal waste water accompanying the waste water surveillance,
- in industrial waste water where biocides are used or produced,
- in projects for soil, sludge, sediment and suspended matter.

For the biocides detectable by HPLC/UV (DIN EN ISO 11369) there are data back to the 1980s. A lot of further substances are regularly measured with calibrated HPLC/MS and GC/MS Systems. The target compound analysis was widened by screenings in the last years, so it is possible to view trends for e.g. Isoproturon, Diuron and Terbutryn over decades. The evaluation according WFD shows, that about 3% surface waters meet the EQS for Diuron. Furthermore Isoproturon, Terbutryn and Terbutylazine are the mainly detected biocides. Organotin-compounds and Naphthalene were often detected in the river Emscher and come probably from industrial sources. The nearly continuous monitoring along the river Rhine allows to depict a higher concentration of a substance running down the river. Unknown substances can be detected to start further research. All data – target monitoring and screening – are published immediately on http://www.elwasims.nrw.de or http://www.lanuv.nrw.de/aktuelles/umwdat.htm.

6.11 Biocide Monitoring in Switzerland

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270 substances are currently authorised in Switzerland for the use as active ingredients in biocidal products (BPD and lists of non-inclusions and notified substances, status 2012). However, a monitoring based nationwide assessment of the water quality relevance of these biocides has been missing. Swiss surface waters are mainly monitored by the 26 cantonal authorities using different approaches. Some of them include pesticides in their monitoring activities, mostly plant protection products (PPPs) but also some biocides.

To gain an overview on pesticide occurrence in Swiss surface waters, monitoring data from cantonal authorities as well as from other sources were collected and analysed for the time period of 2005 to 2012. The pesticide data set contains 563 different sampling sites, mostly located in the Swiss Plateau. Overall 54 different biocides were analysed of which only 18 were exclusively approved for use as biocides, the other 36 compounds were also approved for use in PPP. In comparison, during the same time period almost 150 compounds analysed were exclusively authorised as PPPs. 50% of the 54 biocides were measured at least once above 0.1 µg/l and at least one biocide exceeded this level at more than 50% of the sampling sites. However, for compounds approved for use in both biocide and PPPs it is unclear to which extend the observed contaminations are due to their use as PPPs or as biocides. Furthermore, the monitoring data analysis shows clearly that in small streams higher biocide concentrations are found than in large rivers.

As an addition to the above mentioned data analysis a broad screening of totally 255 PPP and 116 biocides took place at five selected river sites in spring and summer 2012. In order to possibly detect all surface water relevant pesticides the selected sites cover different land use patterns including the most important cultures and also large urban areas. The chemical analysis of the pesticides was done partially as a target (with standards) and as a non-target screening (no standard) by a high resolution mass-spectrometry. The results of this study are expected for mid-2013 and shall support the prioritisation of relevant pesticides to monitor in surface waters in the near future.

6.12 Status of biocides monitoring in France

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In France, monitoring of chemicals in water is being carried out by Water Agencies in the French River Basins. A first state of the art of concentrations of chemicals was done among 2007 to 2009 monitoring data, demonstrating that monitoring was effective for some biocides but that most of the active substances were not covered by routine monitoring.

Following this step, it was decided to specifically include the biocidal active substances in two exceptional monitoring campaigns (for groundwater and surface water, respectively) in order to collect primary information on these substances. The general process for the substances selection to be included in the campaign was based on a prioritisation lead for all types of chemicals not already covered by the 2007-2009 monitoring in order to highlight chemicals of concern. This prioritisation was conducted according to several criteria, among which use, environmental hazard, human health hazard, PBT-like properties, and suspected endocrine disrupting properties. A total of more than 2000 substances were screened allowing highlighting of ca. 300 chemicals, including pesticides, pharmaceuticals, emerging contaminants and 69 biocides. Furthermore, an adaptation was made specifically for French overseas departments with an additional weight given to further biocides, namely insecticides for vector control recommended by WHO.

In a near future, analysis of monitoring campaign should be done with a focus on biocides in order to allow *via* these photographic national campaigns a better detection of biocides active substances in the environment and in order to identify and better predict plausibility of biocides linked environmental risks. In turn, risks possibly identified might serve in feedback regulatory needs if deemed necessary, allowing a better protection of the aquatic environment.

6.13 Biocides in Façades - State of Knowledge

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Biocides are included in organic building façade coatings as protection against algae and fungi growth, but have the potential to enter the environment via wash-off into storm water runoff from wind driven rain. Literature presenting data from experimental studies is scarce; however, diverse studies published environmental impact based on modelling. Monitoring strategies seem to take into account film preservatives and insights to market are of interest. It is time to review current knowledge since science and industry investigated leaching of biocides in coatings for about six years.

The number of substances notified under BPD is significant larger than the number used in market products. Currently, only 3-4 film preservatives are used in significant quantities in organic coatings. The other compounds are negligible or of decreasing importance. Experimental data demonstrate the biocides release as a function of product properties such as biocide properties (Kow, solubility), material composition, embedding, system structure, and environmental factors such as temperature, water contact, and drying between wet periods. The water flux is the fundament of pollutants transport. During exposure to west, an average of about 6% of annual precipitation came off from façade panels with 2 meters height. At higher facades less than 1% was measured. Walls with different orientation show even lower or even no runoff. Consequently, at west and south oriented façades wash-off deliver the biocides to the environment. The release mechanisms of biocides are reflected by a diffusion rate. Wind driven rain wash-off the enriched biocides from coating surface afterwards. Leached biocide concentrations tend to be high early in the coating's lifetime, and then decay with time. Based on the amount remaining in the film after exposure, the occurrence of transformation products, and the amounts in the leachate, degradation plays a role in the overall mass balance. Encapsulated biocides release in the first phase by a reduced kinetics with significant lower concentration. This technology is an excellent example of a “win-win”: the source control measure limit water pollution and producers benefit while maintaining service life. State-of-the-art of biocides application and release behavior will be presented.

Burkhardt, M. et al. (2012): Leaching of Biocides from Façades under Natural Weather Conditions. ES&T, 46, 5497–5503.

Wangler, T.P. et al. (2012): Laboratory scale studies of biocide leaching from building façade materials. B&E, 54, 168-173.

6.14 Monitoring of biocides from urban sources compared to agricultural plant protection products

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Biocides are used mainly in urban environments. However, many compounds used as biocides are chemically identical to plant protection products (PPP) used in agriculture. In terms of monitoring, agricultural plant protection products have so far received much more attention than urban biocides. The aim of the study presented here was to assess simultaneously the importance of urban and agricultural biocide and PPPs.

Substantial part of the biocides are used outdoors and are transported during rain events to surface waters. The same holds true for agricultural PPPs. This study focused on the dynamic during rain events throughout the year in a catchment (25 km^2) with mixed urban and agricultural land use in the Swiss Plateau. Several sub-catchments with various degrees of urban and agricultural land use were studied along with the outlets of a combined sewer overflow, a separate sewer and a wastewater treatment plant.

It was found that concentrations were elevated mostly during rain events. The two exceptions were a) extremely high concentrations peaks in the absence of rain, most likely due to spills, and b) certain compounds which showed elevated background concentrations also during dry periods, indicating that important indoor sources must exist. During rain events, the urban system reacted faster to rainfall than the agricultural system and therefore compounds used as biocides were found mostly in the beginning of rainfall periods. Agricultural losses of PPPs occurred more delayed. Furthermore, biocide losses occurred throughout the year whereas agricultural compounds showed a strong seasonality. Compared to the applied amounts, urban loss rates were up to ten times higher than those of agricultural applications (0.4 to 10% for urban, 0.4 to 0.9% for agricultural compounds). However, some biocides were applied in high amounts, but were never detected. Both sources are important, however there are considerable differences in the dynamics during a rain event as well as throughout the year. These findings help to plan future monitoring strategies and to interpret existing monitoring data.

6.15 Anticoagulant rodenticides in non-target biota in Germany: residues in non-target small mammals

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Anticoagulant rodenticides (ARs) are commonly used to manage commensal rodents such as house mice and Norway rats. Management is required for health protection and hygiene (biocidal use) as well as for the protection of stored agricultural produce (plant protection use). The advantage of ARs is their delayed mode of action that prevents bait shyness in rodents and the availability of the antidote vitamin K. Disadvantages are the potential for resistance to some of the compounds and persistence of compounds that can lead to bioaccumulation in tissue. While there is some knowledge on AR residues in predatory birds and scavengers that consume ARs indirectly via poisoned prey and carrion (secondary poisoning) little is known about AR uptake by non-target small mammal species that directly consume AR bait (primary poisoning). We conduct a monitoring study to quantify AR residues from bait to predators specifically including non-target small mammals during baiting campaigns on farms in NW Germany. Commercially available brodifacoum rolled oat bait is used in autumn and winter. Non-target small mammals are snap-trapped before, at commencement and at the end of 3-week campaigns at different distances from baiting points. Spit pellets of barn owls that live on the farms and prey from barn owl nest boxes are sampled. Samples are screened for 8 registered ARs using high performance liquid chromatography electrospray ionisation tandem mass spectrometry. The content of spit pellets indicates which prey was consumed by owls during baiting. Prey choice in combination with data on species-specific AR residues will help to assess the risk for barn owls when ARs are applied on farms. First results suggest that brodifacoum residues occur specific to non-target species, location (close/away from farm) and season (autumn/winter). Residues of other ARs are rare.

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6.16 Prioritisation of biocides for monitoring campaigns in Switzerland

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In Switzerland cantons are responsible for the surveillance of surface waters. In order to harmonise the monitoring campaigns of the cantons the FOEN (Federal Office for the Environment) started a project for the assessment of micro-pollutants in surface waters. In total roughly 80 compounds from different sources (diffuse and point sources) are selected, for which effect based quality criteria will be derived (AA-EQS, MAC-EQS). The aim is that roughly ten out of these 80 compounds are biocides. The selection of biocides was conducted based on the following requirements: i) the most important sources are represented; ii) the compounds are ecotoxicologycally relevant and/or iii) are measured or expected in high concentrations/loads.

All relevant and available information for the selection of biocides was integrated into a database and a categorisation query was conducted, where all registered biocides (all notified compounds) were classified either as surface water "relevant" or "irrelevant". In the first step of the query compounds for which the 95-percentile of measured concentrations was lower then the numerical (0.1 µg/l) or ecotoxicological quality criterion were judged as "relevant". In the second all others including those without measurements were categorised according to their probability being in the water phase. This was done by a simple approach based on log Kow, half life times and usage of the respective compounds. In the last step the surface water "relevant" compounds defined in the second step were further categorised into those with low ecotoxicological values and those with high.

This categorisation revealed that only 66 out of 381 originally notified biocides are potentially relevant for surface waters according to our procedure. To reduce the selection to ten biocides (e.g. DEET; Terbutryn) additional aspects such as to cover different uses (product types), low ecotoxicological values, different chemical groups or the analytical feasibility were taken into account. At last the selection of compounds is discussed with stakeholders from cantons, other federal offices and industry.

6.17 Analytical challenges for the analysis of biocides in aqueous and solid environmental matrices

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In recent years, biocides have gained increasing interest as so called emerging contaminants, since they are ingredients of various products used in our daily life such as personal care products (PCPs), cleaning agents and paints and coatings. In addition to diffuse sources of agricultural usage, biocides are discharged into the aquatic environment via municipal wastewater treatment plants (WWTPs). Since biocides are biological active compounds, applied to destroy or to inhibit the growth or action of organisms, even low environmental concentrations might have negative impacts on the aquatic environment. As consequence, environmental quality standards (EQS) as low as 0.0025 and 0.065 µg/L are currently suggested for biocides such as irgarol and terbutryn, respectively. Hence, analytical methods have to be designed for the quantification of biocides down to the low ng/L level in surface water and wastewater. As certain biocides such as triclosan and triclocarban have a high affinity for sorption on solid particles, analytical methods are needed enabling the determination of those biocides in activated sludge, suspended matter and sediments.

The objective of this presentation is to illustrate the main challenges for the development and application of LC-MS/MS methods foreseen to determine up to 40 biocides and pesticides in various environmental matrices (surface water, wastewater, activated sludge and sediments). It was found that minimisation and compensation of matrix effects are extremely crucial to ensure a sufficient analytical accuracy and reproducibility. Stable isotope-labelled surrogate standards were appropriate to sufficiently compensate these matrix effects. Without available isotope-labelled surrogate standards, the standard addition method has to be applied or the matrix effects have to be quantified for every analyte/matrix combination to assure an appropriate compensation. Atmospheric pressure chemical ionisation (APCI) and electrospray ionisation (ESI) have been compared regarding their susceptibility for matrix effects. Moreover, a direct injection method without a previous enrichment of the analytes by solid-phase extraction (SPE) is shown as well. Experiences with the environmental monitoring of biocides revealed that concentrations of biocides significantly change over short times indicating that a sufficient time resolution of sampling is the pre-requisition for the determination of annual average concentrations as well as for mass balances in WWTPs and river basins.

6.18 Databases and exchange of monitoring data - experiences from NORMAN

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The NORMAN network is systematically collecting data on the occurrence of non-regulated substances in all environmental matrices and storing them in the EMPODAT database (see www.norman-network.net //Databases //EMPODAT). Biocides represent one of 25 classes of substances identified so far by NORMAN. The database includes a special module for collection of data from bioassays addressing both the (eco)toxicity of environmental samples and (eco)toxicity of individual substances. In 2012 also the use data on numerous emerging substances from Nordic countries became available. The data on the occurrence, (eco)toxicity and use of the substances allow for their prioritisation. The NORMAN Working Group on prioritisation started its work in 2009 and the first prioritisation approaches have already been developed and built into the database as automated procedures. The database contains also an automated procedure for evaluation of data quality based on the provided metadata. At the end of 2011 EMPODAT contained ca. 1 million entries on the occurrence of emerging substances from 25 European countries, however, less than 1% of them were reported on the occurrence of biocides.

The information from non-target screening using mass spectrometry techniques and tools for identification of unknown substances present in complex environmental samples is stored in the NORMAN MassBank portal (accessible via http://massbank.normandata.eu/MassBank/). A new prioritisation procedure of NORMAN non-target screening data has recently been tested in the case study of the Slovak Republic. The approach allows for creating a list of potential candidates to upgrade the current list of emerging substances. Despite the database is still under development, contributions by all NORMAN members and other interested organisations with their GC-EI-MS and LC-MS(MS) accurate mass spectra are strongly encouraged.

The EMPOMAP database collects information on experts-projects-organisations dealing with emerging substances. The database contains, *i.a.*, 119 national and international projects dealing with emerging substances.

As one of its main goals NORMAN network attempts to develop a harmonised approach for collection and interpretation of data on emerging substances in support of European environmental policies. A commonly shared long-term vision of the network members is that NORMAN should become the primary data source and global one-stop-shop for all issues regarding emerging substances contributing to the creation of the early-warning system for emerging pollutants and subsequent policy actions.

7 Abstracts – poster presentations

7.1 Preparation of a prioritisation concept for the monitoring of biocides – Refinement of the data set used for the regulation of biocides

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It is assumed that the entry into force of the European Biocidal Product Directive (BPD) 98/8/EC has effects on the use patterns and environmental discharges of biocidal active substances. A realistic estimation of the actual contamination of the environment with biocidal active substances is a precondition as well as a supportive instrument for an effective and realistic enforcement of the BPD. With the support of data from environmental monitoring programmes it would be possible to review and adjust parameters within the enforcement process, e.g. risk mitigation measures or emission scenarios, which are used during the assessment of biocidal active substances and products. A study concerning the environmental monitoring of biocidal active substances was conducted on behalf of the Federal Environment Agency of Germany in 2011. It included a survey of existing monitoring programmes and studies in the German-speaking countries. This study showed that the data set for the occurrence of biocidal active substances in the environment is insufficient for the evaluation of the actual contamination of environmental compartments and has absolutely to be improved. For this improvement a prioritisation of relevant active substances, specific substance classes or lead components is essential as environmental monitoring including chemical analysis is very cost-intensive. Additionally, not all biocidal active substances can be analysed in the respective laboratories.

The prioritisation concept that is proposed is based on the evaluation of emission characteristics and ecotoxicological effects. The emission characteristics are operationalised by considering the intended use in BPD product types and other indicators. Furthermore, the concept accounts for other properties of the substances being relevant for their distribution in the environment. The concept was tested with 80 biocidal active substances, which are either already included in the annex I of the BPD or currently evaluated under the EU review programme. A check of plausibility was done with the aid of the available monitoring data and prioritisation concepts from other studies.

The results of this study are the basis for the preparation of a monitoring plan, which could be used nationally and internationally, to identify biocidal active substances that are relevant for different environmental compartments. Future monitoring programmes may provide valuable data for the control of existing environmental protection instruments.

7.2 Verification of the success of recent use restrictions for tributyltin by retrospective monitoring of archived biota samples from North and Baltic Sea

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For several decades tributyltin (TBT) was used extensively as antifouling agent in coatings of ships. The high toxicity to aquatic organisms and endocrine effects e.g. on mussels were known since the 1980s. However, the use of TBT-based antifoulants within the European Union was completely banned only 2003. To verify the effectiveness of this measure a retrospective monitoring study was initiated. Appropriate archived samples were retrieved from the German Environmental Specimen Bank (ESB) including standardised homogenate samples of eelpout (*Zoarces viviparus*) and blue mussel (*Mytilus edulis*). The study covered two North Sea and one Baltic Sea locations. Analysis of TBT and its potential degradation products dibutyltin (DBT) and monobutyltin (MBT) was performed by species-specific isotope dilution analysis by GC/ICP-MS. Time series cover the period 1985-2008 (mussel) and 1994-2009 (fish). Until about 2000/2002, TBT levels remained more or less constant (e.g., range 10-20 ng/g wet weight in mussels from the Jadebay/North Sea). After the EU-wide ban of TBT in 2003, however, significant decreases in mussel and fish contamination could be observed. In mussels from the Jadebay, TBT concentrations decreased steadily to about 1 ng/g in 2008 and hence are now below the OSPAR Environmental Assessment Criteria (2.4 ng/g ww). The results demonstrate the effectiveness of the legal measures undertaken to control TBT inputs into the aquatic environment. Nevertheless, TBT is still a relevant pollutant. TBT water concentrations calculated from the tissue concentrations by using respective bioconcentration factors are in the range of Environmental Quality Standards derived in the context of the Water Framework Directive (0.2 ng/L). Thus adverse effects to marine organisms cannot completely be excluded.

7.3 Retrospective monitoring of methyltriclosan in freshwater fish covering the period 1992 - 2008

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Methyltriclosan (MTCS) is a transformation product of the biocide triclosan (TCS) which is commonly used e.g. in personal care products and textiles. Via waste water TCS reaches freshwaters since its degradation in sewage treatment plants (STP) is not complete. Moreover, a fraction of TCS is transformed to MTCS during the STP process. To study levels of the lipophilic MTCS in aquatic biota, muscle of fish (bream, Abramis brama) archived by the German Environmental Specimen Bank were investigated. Standardised annual homogenate samples were analysed by GC/MS directly (MTCS) or after derivatisation (TCS). Fish originated from 17 different German freshwater sites including the rivers Elbe, Mulde, Saale, Rhine, Saar and Danube. The period covered for MTCS was 1992 - 2008.

Since TCS levels were low it was only analysed for the period 1992 - 2003 and 2008 (maximum 69 ng/g TCS in Saar fish in 1998; lipid-based data). TCS and MTCS could not be detected in fish from a reference site (Lake Belau, Northern Germany). However, especially in fish samples from rivers influenced by STP effluents high MTCS were detected (e.g., in Saar bream up to 580 ng/g in 2005). For most sampling sites MTCS concentrations were highest in the period 2002 - 2005. Most time series revealed statistically significant increasing trends of MTCS over a decade until about 2003. However, afterwards levels stayed constant or even decreased at nearly all sites. It is assumed that fish body burdens of MTCS are linked to consumption patterns of TCS. Therefore, the decrease of MTCS is probably a result of a voluntary renunciation of the use of TCS in washing and cleaning agents by the member companies of the German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) as announced in 2001.

7.4 Triclosan and Methyltriclosan in suspended particulate matter – results from the German Environment Specimen Bank (ESB)

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Since the 1990s the environmental appearance of triclosan (TCS) and methyltriclosan (MTCS), the biotransformation product of TCS, is reported. TCS is applied as biocide in personal care products like soaps, shampoos and toothpaste, beside its application in textiles and shoes.

Within the framework of the German Environmental Specimen Bank (ESB) suspended particulate matter (SPM) is collected since 2005 as an additional specimen along with biota (*Abramis brama* and *Dreissena polymorpha*).

Sampling is carried out with sedimentation boxes which are emptied monthly according to the ESB specific Standard Operating Procedure (SOP). The material is characterised on place, sieved and frozen in ice-cuboids after homogenisation. The retrospective analysis of TCS and MTCS of SPM was realised after ultrasonication of the freeze-dried material in n-hexane/acetone (1:1; v/v) and fractionation on silica gel by means of GC-EIMS after derivatisation of TCS with MTBSTFA (Rüdel et al. 2012, Chemosphere, in press).

For a retrospective monitoring stored samples were analysed for TCS and MTCS in *Abramis brama* and SPM, beside a dated sediment core of the ESB. In this contribution data from the monitoring are presented and discussed. Recommendations for future research are provided.

7.5 Long-term monitoring of second-generation anticoagulant rodenticides in non-target wildlife in the UK

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The potential risk of secondary exposure and poisoning associated with the use of second-generation anticoagulant rodenticides (SGARs) is considered to be high, largely because of the acute toxicity and relatively long tissue half-lives of these compounds. In response to conservation concerns over the potential impacts of SGARs on predators in the UK, the Predatory Bird Monitoring Scheme (PBMS: http://pbms.ceh.ac.uk/), a chemical and surveillance monitoring scheme, has monitored exposure to SGARs in various sentinel species, in particular the barn owl (*Tyto alba*) and the red kite (*Milvus milvus*). Residues are quantified in the livers of birds irrespective of cause of death (often traffic collisions and starvation) and so is thought to provide a measure of exposure in the general population.

Recent monitoring data indicate widespread contamination in barn owls and kites. Of birds examined between 2007 and 2010, 173 of 203 (85.2%) barn owls and 55 of 61 (90.2%) red kites had detectable liver concentrations of one or more SGAR. The majority of residues were difenacoum and bromadiolone. These are the most widely used SGARs in Britain and the only ones that can be used outdoors. We have also monitored barn owls over a longer term period and this has shown that exposure, as determined from the % of owls with detectable liver residues, rose from 1983 (the start of monitoring) until approximately 2005, again largely due to increasing exposure to difenacoum and bromadiolone. The proportion of owls with multiple SGARs in their livers has also risen over time. The pattern of exposure since approximately 2005 appears more variable with no clear temporal trend. Spatial analysis of long-term data indicates that the % of owls with detected liver SGAR residues is approximately two-three fold higher in England than in Scotland or Wales, reflecting higher SGAR use in England.

Overall, PBMS monitoring of rodenticides in raptors in Britain provides a key means of determining exposure of wildlife to SGARs and how voluntary and/or mandatory changes in usage affects non-target exposure.

7.6 Monitoring Impacts of Vertebrate Pesticides in the UK: 1993 to 2011

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1. Introduction

Regulatory decisions are made about the suitability of a pesticide for the market after scrutiny of a dossier of studies covering, among other things, efficacy, physical-chemical properties, toxicology and ecotoxicology. It is important, however, once registration is granted, to operate a scheme of impact monitoring to enable modification of use patterns based on practical experience. Post-registration impacts of pesticides in the UK are monitored by the Wildlife Incident Investigation Scheme (WIIS) [1]. Incidents are admitted to the Scheme when there is evidence that a pesticide has caused an adverse effect on wildlife, companion animals, livestock or certain insects. The scheme has been operated by UK government scientists since 1985 and, since 1993, reports have been published with information on individual incidents.

Vertebrate pesticides are used in the UK for the management of a variety of pests including Norway rats (*Rattus norvegicus*), house mice (*Mus musculus*), grey squirrels (*Sciurus carolinensis*) and, formerly, moles (*Talpa europea*). One active substance, alphachloralose, is also used to narcotise birds. The majority of vertebrate pesticides used in the UK, however, are anticoagulant rodenticides. The necessity that vertebrate pesticides possess toxicity to mammals (and rarely birds) results in risks to wildlife. Therefore, non-target causalties of vertebrate pesticides comprise a substantial proportion of WIIS incidents. The Biocidal Products Directive (BPD) is benchmark European legislation published in 1998 to regulate vertebrate pesticides used as biocides [1]. The first products will come to the market in the European Union under its provisions in 2012. It appears timely, therefore, to review the impacts of vertebrate pesticides in the UK, prior to BPD implementation, so that potential effects in reducing non-target casualties may be subsequently observed.

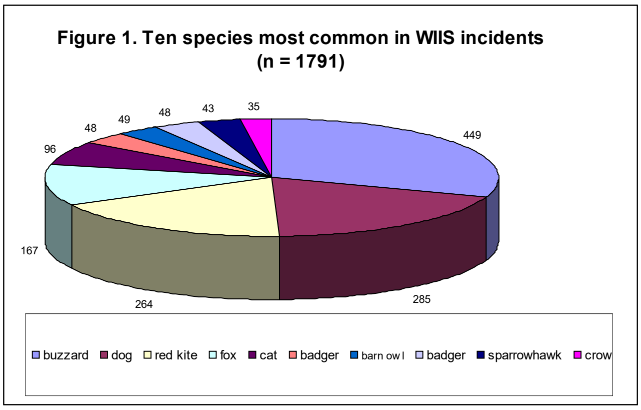
2. Materials and methods

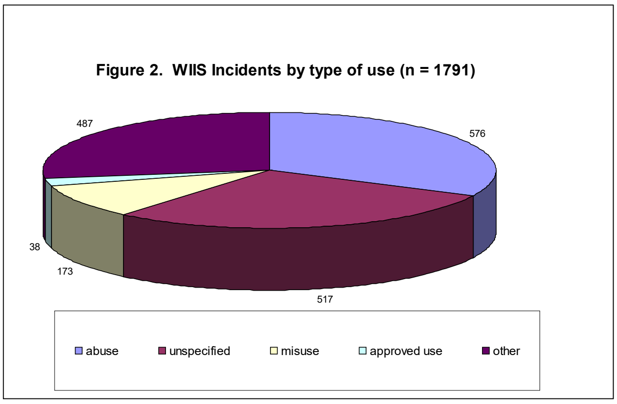
The published annual reports of WIIS were examined and data transposed to a Microsoft Excel spreadsheet. Eight fields were used for each recorded incident: month and year of incident, active substance, species affected, number of individuals, type of casualty (i.e. wildlife, companion animal), whether primary or secondary poisoning was involved, location (county). Within WIIS, each incident is attributed to one of four categories as follows: approved use, misuse, abuse, unspecified. The latter category is used when an incident cannot be attributed to one of the others. During the early years of the Scheme an incident was admitted to the scheme only were obvious harm had been caused and confirmed by finding appropriate symptomology at *post mortem* and tissue pesticide residues. Latterly, and increasingly within the last 4 years, incidents are admitted where carcases of predatory birds and other wildlife are recovered without symptomology, or with other obvious causes of death such as starvation or trauma, but with low-level residues of second-generation anticoagulants. An analysis of WIIS data from 1993 to 2011 is presented here.

3. Results and discussion

A total of 14 vertebrate pesticides was found to have been responsible for 1,791 WIIS incidents in the period. They are (number of incidents in brackets): bromadiolone (514), difenacoum (446), alphachloralose (370), brodifacoum (196), strychnine (89), coumatetralyl (82), warfarin (43), chlorophacinone (28), flocoumafen (9), sodium cyanide (5), aluminium phosphide (4), calciferol (3), coumarin (1), difethialone (1). Several of these active substances were withdrawn in 2006 as a result of the BPD review. Numbers of anticoagulant incidents are approximately proportional to volumes applied, with brodifacoum perhaps over-represented for reasons which are not readily apparent. A wide range of non-target species is involved in WIIS incidents (Figure 1). Among predatory and scavenging birds, buzzards (*Buteo buteo*) and red kites (*Milvus milvus*) predominate. Of the 449 incidents involving buzzards the pesticide(s) found were not thought to have been the principal cause of death in 206 (45.9%); the equivalent value for 264 red kites was 87 (33.0%). Figure 2 shows the distribution of incidents according to type. Sub-lethal residues were found in 487 (27.2%) incidents. The most common were abuse incidents, in which there was purposeful use of a pesticide to cause harm (576 incidents, 31.2%). The most frequent form of this type of incident was the use of alphachloralose put out in meat bait to kill corvids. Buzzards and red kites were often accidental victims in these cases. A further 173 (9.7%) incidents are caused by pesticide misuse. Only 38 (2.1%) incidents, and none within the last 3 years, were caused when pesticides were used according to label instructions. A large number of incidents could not be allocated to one of these three categories (n=517, 28.9%), and many of these involved anticoagulants. These active substances have a chronic mode of action and casualties are often found far from the location of exposure, making causal investigation difficult. However, there is no reason to suspect that these incidents are distributed between the three other types (abuse, misuse, approved use) in a proportion that is different from those for which a cause is found. If the 'unspecified' incidents are allocated for in the same proportion, we arrive at a total of 98 approved use incidents over the 19-year period of the analysis. This low level affords some confidence that, used according to label instructions, vertebrate pesticides, including anticoagulant rodenticides, pose no significant acute risk to non-targets in the UK.

A criticism sometimes levelled at the WIIS is that it under-records incidents. This is obviously true as there is no doubt some casualties are not found. But, with more than 32 years of continuous WIIS operation, it would have been apparent if there was a failure to detect a major impact on an important wildlife species. It may be significant that populations of the two species of predatory/scavenging birds most frequently found in WIIS incidents, buzzard and red kite, are currently expanding rapidly in the UK. There is no room for complacency, however, because other studies such as those conducted by the UK Predatory Bird Monitoring Scheme (PBMS) show that exposure of wildlife to anticoagulants in the UK is widespread [3]. Mitigation is required urgently to reduce this contamination [4]. Schemes such as WIIS and PBMS will be important in monitoring impacts of pesticides as the European Commission's Sustainable Use Directive (SUD) [5] is implemented. Within the SUD, a system of risk indicators is applied so that the benefits of the legislation are apparent in the improved health of man and the environment. Monitoring schemes such as WIIS, clearly offering direct and specific risk indicators, will play an important part.





4. Conclusions

The operation of the WIIS is an important measure for monitoring impacts of pesticides on non-target wildlife and companion animals in the UK. Incidents caused by vertebrate pesticides mainly involve wildlife crime. The rarity of incidents occurring when vertebrate pesticides are used correctly affords some confidence that current use patterns are broadly correct. However, the frequency and breadth of wildlife incidents involving the anticoagulant rodenticides, and widespread low-level residues, is a continuing concern that requires vigilance and the rigorous application of a range of mitigation measures [4].

5. References

[1] European Community 1998. Directive 98/8/EC of the European Parliament and of the Commission of 16 February 1998 concerning the placing of biocidal products on the market. Official Journal of the European Communities L 123/1: 63 pp.

[2] Health and Safety Executive 2010. Wildlife Incident Investigation Scheme. http://www.pesticides.gov.uk/environment.asp?id=58. Accessed 25.11.11.

[3] Walker LA, Llewellyn NR, Peréira MG, Potter ED, Sainsbury AW and Shore RF 2010. Anticoagulant rodenticides in predatory birds 2009: a Predatory Bird Monitoring Scheme (PBMS) report. Centre for Ecology & Hydrology, Lancaster, UK. 17pp.

[4] Campaign for Responsible Rodenticide Use 2011. http://www.thinkwildife.org.uk. Accessed 25.11.11.

[5] European Community 2009. Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for the sustainable use for Community action to achieve sustainable use of pesticides. Official Journal of the European Communities L 309/71: 16 pp.

7.7 Non-target screening analyses of organic contaminants in river systems as a base for monitoring measures

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Organic contaminants discharged to the aquatic environment exhibit a high diversity with respect to their molecular structures and the resulting physico-chemical properties. The chemical analysis of anthropogenic contamination in river systems is still an important feature, especially with respect to (I) the identification and structure elucidation of novel contaminants, (ii) to the characterisation of their environmental behaviour and (iii) to their risk for natural systems.

A huge proportion of riverine contamination is caused by low-molecular weight organic compounds, like pesticides plasticisers, pharmaceuticals, personal care products, technical additives etc. Some of them, like PCB or PAH have already been investigated thoroughly and, consequently, their behaviour in aqueous systems is very well described. Although analyses on organic substances in river water traditionally focused on selected pollutants, in particular on common priority pollutants which are monitored routinely, the occurrence of further contaminants, e.g. biocides, pharmaceuticals, personal care products or chelating agents has received increasing attention within the last decade. Accompanied, screening analyses revealing an enormous diversity of low-molecular weight organic contaminants in waste water effluents and river water become more and more noticed. Since many of these substances have been rarely noticed so far, it will be an important task for the future to study their occurrence and fate in natural environments. Further on, it should be a main issue of environmental studies to provide a comprehensive view on the state of pollution of river water, in particular with respect to lipophilic low molecular weight organic contaminants. However, such non-target-screening analyses has been performed only rarely in the past.

Hence, we applied extended non-target screening analyses on longitudinal sections of the rivers Rhine, Rur and Lippe (Germany) on the base of GC/MS analyses. The investigations revealed complex pattern of anthropogenic contaminants comprising a lot of still unnoticed pollutants (e.g. specific sulfones, trifluoromethyl substituted substances, nitrogen heterocycles etc.) or still unidentified compounds (such as selected brominated aromatics) of obviously high environmental relevance. A selection of several different contaminants will be discussed in detail comprising their emission sources, their emission behaviour, their fate within the river water bodies and in particular their structural properties.

Generally, this investigation demonstrated the need to expand our analytical focus on a broader spectrum of organic contaminants, in particular to build up an adapted base for advanced monitoring studies.

7.8 The use of experimental data to estimate long term biocide leaching ratios from wooden facades

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In this study some of the problems by using experimental leaching data to predict long term leaching values are highlighted.

As an example of a façade treated with biocide we used data from a long term emission study where copper was used as the main biocide in preservative treated wood above ground not covered (Use Class Class 3 scenario). Treated boards were exposed vertically above ground to natural weather conditions according to NT Build 509 (2005). The study included two systems; an amine copper ACQ-type formulation, air-dried after treatment, and the same formulation which was hot oil vacuum dried after treatment. Both systems were vacuum-pressure treated to a product retention of 22 kg/m^3. During a six year study period run-off emissates were continuously collected and their content of copper determined by chemical analysis at intervals. The total emission of copper was approximately 2 g/m^2 exposed wood for the ACQ treated air dried boards, whereas the hot oil vacuum dried boards had a copper emission which was ten times lower at 0.2 g/m^2 in total after six years.

A number of calculations were made based on the Emission Scenario Document (ESD) for PT 8 (wood preservative) within the BPD.

The prediction of long term emission (Time 2) was highly influenced by the type of extrapolation used.

For the air-dried system a linear extrapolation gave the best fit (highest R2 value) both using two and six years of data (excluding the initial leaching). However, using a logarithmic extrapolation gave lower R^2 values, but consistent long term leaching estimates using all data within each period. In this case two years of leaching data was sufficient to create a reliable estimate. The consequences for the air-dried ACQ treated set-ups after 20 years of exposure are outlined in the table below.

Air dried ACQ	Type of curve fit	R^2	20 years (mg Cu/m^2) data normalized to 700 mm rain/year	% of initial Cu content
2 years	Logarithmic	0.950	2758	10.1
6 years	Logarithmic	0.982	2821	10.3
2 years*	Linear	0.998	9871	36.1
6 years**	Linear	0.999	4629	16.9

*excluding the first six months
**excludning the first two years

Thus, these results indicate that for systems with a high initial release of biocides the use of linear extrapolation may result in high and unrealistic estimates, while logarithmic extrapolations may result in more realistic estimates. For systems with a constant release of biocides the best fit tends to be a linear extrapolation.

7.9 Dynamics of biocide emissions from buildings in a suburban stormwater catchment

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Biocides such as terbutryn and carbendazim are used to protect the façade surfaces of the buildings, would it be painted render or wood. These biocides can be mobilised from the materials if rainwater gets into contact with them. Hence, these biocides will be found in rainwater runoff (stormwater) that is traditionally managed as clean water. Within this 9 month study the biocide emissions in a small suburban stormwater catchment were analysed with respect to concentrations, mass loads and dynamics. It could be demonstrated that the median concentrations were relatively high (around 100 ng L^{-1}) while in peak events concentrations were reaching up to 1800 ng L^{-1}. The concentrations were highest for terbutryn and carbendazim (100 ng L^{-1}), while the concentrations for isoproturon, diuron, iodocarb, dichloro-N-octylisothiazolinone, N-octylisothiazolinone, benzoisothiazolinone, cybutryne, propiconazole, tebuconazole, mecoprop and 2,6-dichlobenzamide were one order of magnitude lower. Emissions turned out to be 14 μg m^{-2} $event^{-1}$. First flush phenomena have only been observed in some selected events, while usually the concentrations were evenly distributed over the rain event.

7.10 Emission Scenario Documents (ESD) for biocidal products: Data refinement via questionnaires

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The authorisation process for biocidal products requires a thorough exposure estimation and risk assessment for the environment and human health. In order to build a harmonised basis for environmental exposure calculations according to directive 98/8/EG for all European member states, emission scenario documents (ESDs) for various product types have been developed. Here, a methodology for estimating quantities of active substances that may be released to the environment is displayed. For human exposure a similar approach is planned: HESD (human exposure scenario documents). However, in special cases the given default scenarios do not reflect realistic application situations.

Using a questionnaire, a survey was performed to collect data for the application of disinfectants on eggs in poultry hatcheries. Within such a questionnaire it must be possible to reproduce even this very complex application scenario. The results from this survey are described and compared with default values in the ESD. An exemplary calculation is performed to demonstrate the expected differences in exposure estimations on the different data bases. In addition, the given information about the application is valid and useful for human exposure as well. Altogether, these data show very clearly the importance of an ongoing discussion and regularly exchange of information with the downstream users of biocidal products, in particular to consider the progress in application techniques. In addition, the use of older data always poses a risk of misinterpretation and apparently minor differences in parameters could have major consequences for risk assessments.

In a regulatory context these results show the demand for periodical up-dates and re-evaluations of ESDs as well as the need for the possibility of refinement and a flexible and adequate implementation. ESDs should be understood as presenting exemplarily models that have to be handled as living-documents in order to remain up to date; data re-evaluation and data collection reveals itself as an irreplaceable instrument. After all, it has to be considered that the estimation of environmental exposure is a major part of the risk assessment process eventually determining whether the application of a biocidal product is expected to be safe or not.

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Umweltforschungsplan des
Bundesministeriums für Umwelt,
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UBA-FB-00

Überprüfung, Überarbeitung und Vervollständigung des vorläufigen Priorisierungs-/Monitoring-Konzepts (Annex 2)

Teilbericht zum Projekt: Umweltbelastung durch Biozide: Erarbeitung der Eckpfeiler eines Monitoring-Messprogrammes für Einträge von Bioziden in die Umwelt

von

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Im Auftrag des Umweltbundesamtes

Mai 2014

Kurzbeschreibung

In diesem Projekt wurde ein Konzept für die Priorisierung von Biozidwirkstoffen für ein Umweltmonitoring optimiert. Die dafür berücksichtigten Biozide sind Verbindungen, für die (öffentlich oder vertraulich) EU Biozid-Bewertungsberichte als primäre Datenquellen zur Verfügung standen. Die Biozidwirkstoffe werden entweder derzeit im EU-Biozid-Altwirkstoffprogramm geprüft oder sind bereits nach der EU-Biozid-Produkte-Verordnung (Nr. 528/2012) zugelassen. Häufig enthalten die Bewertungsberichte auch Angaben und Daten zu potenziellen Transformationsprodukten (TPs). Insgesamt wurden ca. 170 Verbindungen einschließlich der TPs in diesem Priorisierungsansatz berücksichtigt. Das vorgeschlagene Priorisierungsschema besteht aus mehreren Schritten. In einem ersten Schritt werden die Stoffe hinsichtlich möglicher direkter oder indirekter Emissionen in Umweltmedien bewertet (vor allem basierend auf dem Verwendungszweck in bestimmten Biozid-Produktarten und deren Relevanz für Emissionen in Umweltmedien). Zusätzlich werden verfügbare Informationen zum Verbrauch, beispielsweise operationalisiert als Anzahl der in Deutschland registrierten Produkte mit dem entsprechenden Biozid, genutzt. Der zweite Schritt umfasst die Beurteilung möglicher schädlicher Auswirkungen der Biozidwirkstoffe auf Basis von Daten aus den Bewertungsberichten (z.B. PNECs). Im dritten Schritt wird die Relevanz der Biozidwirkstoffe für die Überwachung in verschiedenen Umweltkompartimenten beurteilt (z.B. Wasserphase, Schwebstoffe, Biota). Je nach Kompartiment werden in diesem Schritt relevante stoffspezifische Eigenschaften wie die Verteilung zwischen den Umweltmedien, die Persistenz bzw. die Bioakkumulation betrachtet. Für jedes Kompartiment wurde eine Liste der als relevant priorisierten Biozide abgeleitet. Die erhaltenen kompartimentspezifischen Priorisierungslisten werden anhand verfügbarer Biozidmonitoring-Daten diskutiert. Bei der Bewertung der Monitoringdaten ist jeweils zu prüfen, ob die Wirkstoffe auch im Rahmen anderer Regelungen angewendet werden (z.B. als Pflanzenschutzmittel). In diesen Fällen ist es häufig nicht möglich, Umweltfunde einer spezifischen Nutzung zuzuordnen. Folglich konzentriert sich die Auswertung in erster Linie auf Monitoringdaten von Stoffen, die nur als Biozide zugelassen sind.

Abstract

In this project a concept for the prioritisation of biocidal substances for an environmental monitoring was optimised. The set of covered biocides included compounds for which (public or confidential) EU biocide assessment reports as primary data source were available. These biocides are either in the EU biocides review programme or already approved according to the EU Biocidal Product Regulation (No. 528/2012). Often also data on potential transformation products (TPs) are given in the assessment reports. In total about 170 compounds including TPs were covered by the prioritisation approach. The proposed prioritisation scheme consists of several steps. In a first step compounds are evaluated for potential direct or indirect emissions into environmental media (mainly based on the intended use in certain biocide product types and their relevance for environmental media). Additionally, available information on consumption, operationalised, e.g. as number of registered products with the respective biocide in Germany, is applied. The second step covers the assessment of the potential to cause adverse effects based on data available from the assessment reports (e.g., PNECs). In a third step the relevance of biocides for monitoring in an environmental compartment (e.g., water phase, suspended particulate matter, biota) is scored. Depending on the compartment, substance-specific properties relevant for partitioning between compartments, persistence and/or bioaccumulation are considered. Finally, for each compartment a list of prioritised biocides was derived. The final compartment-specific prioritisation lists are discussed with regard to available biocide monitoring data. In the assessment of monitoring data it has also to be considered whether the compounds are also applied under other regulations (e.g., as plant protection products). In these cases it is often not possible to allocate environmental findings to a specific usage. Consequently, the evaluation has to focus primarily on monitoring data of compounds solely approved as biocides.

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Abkürzungsverzeichnis

AF	Assessment-Faktor
AMIS	Arzneimittelinformationssystem
AP	Arbeitspaket
AZM	Arzneimittel
BAuA	Bundesanstalt für Arbeitsschutz und Arbeitsmedizin
BCF	Biokonzentrationsfaktor (bioconcentration factor); als L/kg bestimmt (wird zur besseren Übersichtlichkeit teilweise ohne Einheit angegeben)
BG	Bestimmungsgrenze
BIT	1,2-Benzisothiazolin-3(2H)-on
BPR	Biozidprodukte-Verordnung (Verordnung (EU) Nr. 528/2012)
CAS Nr.	internationaler Bezeichnungsstandard für chemische Stoffe (CAS = Chemical Abstracts Service)
CLP	Verordnung (EG) Nr. 1272/2008 über die Einstufung, Kennzeichnung und Verpackung von Stoffen und Gemischen (Regulation on Classification, Labelling and Packaging of Substances and Mixtures)
DCOIT	4,5-Dichlor-2-octyl-2H-isothiazol-3-on
DEET	N,N-Diethyl-m-toluamid
DIMDI	Deutsches Institut für Medizinische Dokumentation und Information
DMSA	N,N-Dimethyl-N'-phenylsulfamid (Dichlofluanid TP)
DMST	N,N-Dimethyl-N'-p-tolylsulfamid
EINECS Nr.	Nummer von Stoffen im Altstoffverzeichnis der EU (European Inventory of Existing Commercial Chemical Substances)
ESIS	Europäisches Chemikalien-Informationssystem (European chemical Substances Information System)
EU	Europäische Union
FG	Frischgewicht/Feuchtgewicht
GUS	Groundwater Ubiquity Score (Indikator zur Grundwassergefährdung)
HG	Hauptgruppe (von Biozid-Produktarten)
HPVC	Chemikalie, die in Mengen von › 1000 Tonnen pro Jahr produziert wird (high production volume chemical)
IME	Institut für Molekularbiologie und Angewandte Oekologie (Fraunhofer IME)
IPBC	3-Iod-2-propynylbutylcarbamat
k.A.	keine Angabe
K_{OC}	Verteilungskoeffizient organischer Kohlenstoff-Wasser eines Stoffes
K_{OW}	Verteilungskoeffizient n-Oktanol-Wasser eines Stoffes
LAWA	Bund/Länder-Arbeitsgemeinschaft Wasser

log	dekadischer Logarithmus
LPVC	Chemikalie, die in Mengen von 10 - 1000 Tonnen pro Jahr produziert wird (low production volume chemical)
MIT	2-Methyl-4-isothiazolin-3-on
MITC	Methylisothiocyanat (Dazomet TP)
OGewV	Oberflächengewässerverordnung
PA	Produktart von Bioziden
PEC	abgeschätzte Umweltkonzentration (predicted environmental concentration)
PNEC	Konzentration eines Stoffes, bei der keine Schädigung eines Organismus zu erwarten ist (predicted no effect concentration)
PBT	persistent, bioakkumulierend, toxisch (gemäß bestimmter Kriterien)
PSM	Pflanzenschutzmittel
QAV	quartäre Ammoniumverbindungen
QSAR	Quantitative Struktur-Aktivitätsbeziehungen (quantitative structure activity relations)
REACh	Registration, Evaluation, Authorisation and Restriction of Chemicals
SGAR	Antikoagulantien-Rodentizide der zweiten Generation (second-generation anticoagulant rodenticides)
TBT	Tributylzinn (Kation; in Produkten unterschiedliche Gegenionen möglich)
TP	Transformationsprodukt
UBA	Umweltbundesamt
UPB	Umweltprobenbank
UQN	Umweltqualitätsnorm
vB	stark bioakkumulierend (very bioaccumulative) nach definierten Kriterien
vP	sehr persistent (very persistent) nach definierten Kriterien
WRRL	Wasserrahmenrichtlinie

Hinweis zu den Datentabellen

Die Daten wurden sorgfältig recherchiert und geprüft. Allerdings könnten in Einzelfällen Übertragungsfehler vorliegen, da die Datenwerte manuell in die Tabellen übertragen werden mussten.

Entscheidungen über die Zulassung / Nichtzulassung von Bioziden gemäß Biozidprodukte-Richtlinie für die Verwendung in bestimmten Produktarten, die vor April 2014 getroffen wurden, konnten berücksichtigt werden. Eine Nichtzulassungsentscheidung für eine Produktart kann die Beurteilung des jeweiligen Biozids (Priorisierung für das Umweltmonitoring) verändern.

Auszug Leistungsbeschreibung: Arbeitspaket III

Im Vorgängerprojekt (Rüdel und Knopf 2012) wurde ein Entwurf für ein Priorisierungskonzept entwickelt und für die einzelnen Umweltkompartimente (terrestrische und aquatische Kompartimente inkl. Biota, Atmosphäre, Kläranlagen) auf Basis einer begrenzten Anzahl von Biozidwirkstoffen, für die Daten vorlagen, bereits erste Monitoring-Kandidaten identifiziert. Ziel dieses Arbeitspaketes ist, den Konzeptentwurf zu überprüfen, wenn notwendig zu korrigieren und zu vervollständigen. Während der Erstellung des Gutachtens und während der Abschlusspräsentation am UBA wurden bereits folgende Punkte identifiziert, für die eine Überprüfung oder Verfeinerung in Frage kommt:

PBT-Kriterien: Auf welcher Stufe der Priorisierung sollen diese Eigenschaften geprüft werden? Ist für das zu entwickelnde Monitoring-Konzept eine kompartimentspezifische Betrachtung des P-Kriteriums notwendig? Derzeit wird die Persistenz im vorgeschlagenen Konzept unabhängig vom Kompartiment als ein Aspekt der Priorisierung verwendet. Es soll geprüft werden, ob es zielführender ist, die Bewertung für die Persistenz (P/vP) für die jeweils relevanten Kompartimente durchzuführen (Wasser, Sediment, Boden).

Die Emissionsmenge biozider Wirkstoffe ist neben der ökotoxikologischen Relevanz als Hauptkriterium für die Priorisierung identifiziert worden. Emissionsmengen für relevante Wirkstoffe konnten im Vorgängerprojekt nur unzureichend ermittelt werden. Aus diesem Grund erfolgte eine grobe Einschätzung über die Anzahl wirkstoffrelevanter PA, aktuell gemeldeter Produkte im BAuA-Melderegister, Produktions- und Importmengen (ESIS-Datenbank) und eine eventuell parallele Verwendung als Arznei- oder Pflanzenschutzmittel. Fraunhofer IME bietet an, für identifizierte Monitoring-Kandidaten Verbrauchsmengen bei Industrieverbänden und Herstellern strukturiert zu erfragen. Vom Umweltbundesamt gegebenenfalls zur Verfügung gestellte Daten werden ebenfalls berücksichtigt. Es wird auch geprüft, ob kommerzielle Marktstudien für diesen Zweck nutzbar sind. Auf Grundlage der hier ermittelten Verbrauchsdaten wird die Kandidatenliste gegebenenfalls überarbeitet.

Es wird geprüft, inwieweit die Gewichtung der einzelnen Aspekte bei der Priorisierung optimiert werden sollte (z.B. auf Basis einer Sensitivitätsanalyse). Gegebenenfalls sollte z.B. die Wichtung der Relevanz der auf Basis der Biozid-Produktarten bewerteten Emissionsrelevanz für bestimmte Umweltkompartimente (Schritt 3) angepasst werden.

Im Vorgängerprojekt konnte das Priorisierungskonzept nur anhand eines Testdaten-satzes von ca. 120 Wirkstoffen überprüft werden. Bei diesen Bioziden handelt es sich vorwiegend um Wirkstoffe der ersten und zweiten Prioritätenliste des Altwirkstoff-verfahrens, die bereits im Review-Verfahren gemäß Biozidprodukte-Richtlinie (RL 98/8/EG) bearbeitet wurden und für die dem UBA Daten aus der Risikobewertung vorliegen. Mit Hilfe des UBA wird der Forschungsnehmer das Priorisierungskonzept für alle relevanten Wirkstoffe im Review-Verfahren (d.h., z.B. ohne Metallsalze sowie auch natürlich vorkommende Stoffe und anorganische Chlorverbindungen) überprüfen. Das UBA wird den Forschungsnehmer unterstützen, indem es andere EU-Mitgliedsstaaten bittet, die verfügbaren Daten aus der vorläufigen Risikobewertung für dieses Projekt zur Verfügung zu stellen.

Abschließend sollen unter Berücksichtigung aller relevanten notifizierten Wirkstoffe Monitoring-Kandidaten für alle Umweltkompartimente identifiziert und priorisiert werden (Listen prioritärer Biozide für alle relevanten Umweltkompartimente).

1 Zusammenstellung relevanter Umweltkompartimente für ein Biozidmonitoring

Als Basis für die spätere Priorisierung wurden zunächst relevante Umweltkompartimente identifiziert. Hierbei wird zum einen auf die Auswertung im Vorprojekt (Rüdel und Knopf 2012) zurückgegriffen. Dort wurden die relevanten Kompartimente (Wasser, Boden, Luft) auf Basis des Einsatzes je nach Produktart bewertet, wobei eine Untersuchung im Auftrag der EU als Basis diente (COWI 2009). Zum anderen dient die Auswertung der recherchierten Monitoring-Daten (siehe AP II) als Grundlage für die Auswahl.

In der Studie von COWI (2009) wurden Bewertungen hinsichtlich der möglichen Umweltauswirkungen durch den Einsatz von Biozidwirkstoffen in Abhängigkeit vom Einsatzgebiet (d. h. PA) und der professionellen Anwendung bzw. der Anwendung durch nicht-professionelle Nutzer aufgeführt. Dabei wurde zwischen potenziellen Umweltbelastungen der Umweltmedien in der Anwendungsphase (meistens kurz) und der Nutzungsphase (meistens deutlich länger als die Anwendungsphase) differenziert. Diese Auswertung wird hier als Ausgangspunkt genutzt.

Tabelle 1 zeigt die aggregierten Ergebnisse der qualitativen Einschätzungen je PA für direkte und indirekte Umwelteinträge von Bioziden aus Anwendungs- und Nutzungsphase nach COWI (2009), die aufgrund der Erfahrungen des Umweltbundesamtes (UBA) angepasst wurde. So werden beispielsweise potentiell abwasserrelevante PA (z.B. PA 8, 10, 18, 19) in der Untersuchung von COWI (2009) nicht entsprechend berücksichtigt (d.h. Kategorie „keine Relevanz von Umwelteinträgen über Kläranlagen“). Bei der Bewertung bezüglich der Relevanz dieses Aspekts wurden diese vier PA zwar zunächst als in der Anwendungsphase kläranlagenrelevant eingestuft. Die Beurteilung der Nutzungsphase in COWI (2009) ergab aber keine Kläranlagenrelevanz (bzw. für PA 19 nur eine geringe). Da die Nutzungsphase anscheinend stärker gewichtet wurde, sind diese PA insgesamt als nicht relevant für Einträge in Kläranlagen eingestuft worden. Auf Basis der Expertise des Umweltbundesamtes werden diese PA in der Übersicht zusätzlich berücksichtigt.

Tabelle 1: Übersicht über die Relevanz potenzieller Umwelteinträge von Bioziden in Abhängigkeit von der Produktart; die Verbrauchsmenge wurde bei der Abschätzung der Umwelteinträge nicht berücksichtigt (Auszug aus COWI 2009; Produktarten-Bezeichnungen beziehen sich auf die aktuelle Biozidverordnung EU/528/2012; in den schattierten Feldern wurden die Bewertungen wurden aufgrund der Erfahrungen des Umweltbundesamtes angepasst).
XXX hohe Relevanz, XX mittlere Relevanz; X niedrige Relevanz; - vermutlich nicht relevant.

	Biozid-Produktart – Beschreibung	Jährliche Verbrauchsmenge	Direkte Umwelteinträge	Umwelteinträge über Kläranlagen
	Hauptgruppe 1: Desinfektionsmittel			
PA 1	Menschliche Hygiene	XXX	-	XX
PA 2	Desinfektionsmittel und Algenbekämpfungsmittel, die nicht für eine direkte Anwendung bei Menschen und Tieren bestimmt sind	XXX	X	XXX
PA 3	Hygiene im Veterinärbereich	XXX	X	XX
PA 4	Lebens- und Futtermittelbereich	XXX	-	XXX
PA 5	Trinkwasser	XXX	X	X
	Hauptgruppe 2: Schutzmittel			
PA 6	Schutzmittel für Produkte während der Lagerung	XX	X	X
PA 7	Beschichtungsschutzmittel	XX	XX	XX
PA 8	Holzschutzmittel	XXX	XX/XXX	X
PA 9	Schutzmittel für Fasern, Leder, Gummi und polymerisierte Materialien	XX	X	X
PA 10	Schutzmittel für Baumaterialien	XXX	XX	XX
PA 11	Schutzmittel für Flüssigkeiten in Kühl- und Verfahrenssystemen	XXX	XX	XX
PA 12	Schleimbekämpfungsmittel	XX	XX	XX
PA 13	Schutzmittel Bearbeitungs- und Schneideflüssigkeiten	XX	-	X
	Hauptgruppe 3: Schädlingsbekämpfungsmittel			
PA 14	Rodentizide	X	XX	X
PA 15§	Avizide	-	XX	-

	Biozid-Produktart – Beschreibung	Jährliche Verbrauchsmenge	Direkte Umwelteinträge	Umwelteinträge über Kläranlagen
PA 16#	Bekämpfungsmittel gegen Mollusken und Würmer und Produkte gegen andere Wirbellose	-	XXX	-
PA 17§	Fischbekämpfungsmittel	-	XXX	-
PA 18	Insektizide, Akarizide und Produkte gegen andere Arthropoden	XXX	XXX	XXX
PA 19	Repellentien und Lockmittel	XX	XX	XX
PA 20§	Produkte gegen sonstige Wirbeltiere (vorher Produktart 23 nach Biozidprodukte-Richtlinie)	-	XX	-
Hauptgruppe 4: Sonstige Biozidprodukte				
PA 21	Antifouling-Produkte	X	XXX	-/X
PA 22	Flüssigkeiten für Einbalsamierung und Taxidermie	X	X	X

kein Biozidwirkstoff für diese PA im Review-Programm; § in Deutschland ist gemäß der Verordnung über die Zulassung von Biozid-Produkten und sonstige chemikalienrechtliche Verfahren zu Biozid-Produkten und Biozid-Wirkstoffen von 2002, zuletzt geändert 2006, keine Zulassung für diese PA vorgesehen.

In der weiteren Betrachtung werden Produktarten, die in Deutschland nicht für eine Zulassung vorgesehen sind, nicht weiter berücksichtigt (PA 15, 17, 20).

Als relevant werden hier alle PA eingestuft, denen in der obigen Tabelle für den entsprechenden Pfad (direkt, indirekt) eine hohe (XXX) oder mittlere (XX) Relevanz zugeordnet wird: PA 1, 2, 3, 4, 7, 8, 10, 11, 12, 14, 16, 18, 19, 21.

Weiterhin sind nach COWI (2009) und Expertenwissen des UBA Biozidwirkstoffe aus den folgenden Produktgruppen aufgrund möglicher direkter Umwelteinträge insbesondere relevant für die folgenden Umweltmedien:

Oberflächengewässer: PA 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 (Hinweis: ein direkter Eintrag in die marine Umwelt erfolgt für PA 11, 12, 21);

Böden: PA 7, 8, 10, 14, 18, 19;

Atmosphäre: PA 8, 11, 14, 18.

Relevante PA für indirekte Einträge über Kläranlagen in die Umwelt (Wasser bzw. Boden) sind: PA 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 (siehe auch die Hinweise im nächsten Absatz).

Hinsichtlich der Einträge in Böden ist anzumerken, dass bei COWI (2009) nicht zwischen direkten und indirekten Bodeneinträgen unterschieden wird. Indirekte Einträge erscheinen z.B. relevant für PA 3 (Biozidprodukte für die Hygiene im Veterinärbereich) und PA 18 (u.a. Stallinsektizide) bei landwirtschaftlicher Gülleausbringung. Für PA 3 wird dieser Pfad im COWI-Bericht (COWI 2009, Annex 1) grundsätzlich auch thematisiert, führt aber nicht zu einer entsprechenden Bewertung. Die indirekte Belastung von Böden durch eine landwirtschaftliche Klärschlamm-Nutzung wird bei COWI (2009) nicht als relevant bewertet.

Zusammenfassend ist davon auszugehen, dass Oberflächengewässer aufgrund der Anwendungsmuster von Bioziden in den meisten Fällen die relevanteste Matrix für potenzielle Umwelteinträge sind (entweder durch direkte oder indirekte Einträge; sowohl während der Anwendung als auch der Nutzungsphase). Dies gilt insbesondere für Anwendungen in Haushalten, wo Biozide über das Abwasser in Kläranlagen gelangen. In der Kläranlage erfolgt in den meisten Fällen eine mehr oder weniger starke Eliminierung, die u.a. vom Abbau- und Sorptionsverhalten der Biozide abhängig ist. Direkte Einträge in Böden erscheinen nur für einige PA relevant und sind vermutlich in den meisten Fällen lokal begrenzt (z.B. Holzschutzmittel, Rodentizide). Dies kann jedoch langfristig zu einer (regionalen) Gefährdung für das Grundwasser führen. Relevanter erscheinen dagegen indirekte Einträge sorbierter Biozide in Böden über die Klärschlammausbringung (soweit diese in Deutschland noch erfolgt) oder über die Nutzung von Gülle, die Rückstände von Bioziden enthalten kann, in der Landwirtschaft. Belastungen der Umgebungsluft erscheinen insbesondere während der Anwendung möglich, sind aber eher lokal begrenzt und aufgrund der atmosphärischen Durchmischung vermutlich nicht großräumig relevant. Ein Schwerpunkt eines Umweltmonitoring auf Biozide liegt somit auf (Oberflächen)-Gewässern.

Tabelle 2 zeigt, wie relevant die verschiedenen Kompartimente nach den Ergebnissen der im Vorläuferprojekt durchgeführten Umfrage bei Institutionen, die an Monitoring-Programmen beteiligt sind sowie anhand der Literaturrecherche für ein Biozidmonitoring einzuschätzen sind (aktualisiert und erweitert um Literatur aus anderen europäischen Staaten, siehe AP II; auf Basis der Auswertung in Rüdel und Knopf 2012).

Tabelle 2: Für ein Biozidmonitoring relevante Umweltkompartimente mit Beispielen für nachgewiesene Stoffe. Zusammenstellung anhand der Ergebnisse der Umfrage bei Monitoring-Institutionen und der Literaturrecherche (auf Basis der Auswertung in Rüdel und Knopf 2012; aktualisiert und erweitert um Literatur aus anderen europäischen Staaten).
X nur einzelne Daten/Angaben, kein systematisches Monitoring; XX Datenbasis für eine Reihe von Stoffen; XXX gute Datenbasis für viele Stoffe, systematisches Monitoring; - keine Daten/Angaben.

Matrix	Relevante Produktarten	Relevant gemäß Monitoring-Daten	Beispiele nachgewiesener Stoffe/ Konzentrationsdaten › BG
Oberflächenwasser - marin (Marinas/küstennah)	PA 11, 12, 21	XX	Diuron§#, Cybutryn, Dichlofluanid§#, Chlorthalonil§#, DCOIT
Sedimente - marin (Marinas/küstennah)		XX	Cybutryn, Dichlofluanid§#, Chlorthalonil§#
Aquatische Organismen - marin (Marinas/ küstennah)		X	Cybutryn
Oberflächenwasser - limnisch (direkt)$	PA 7, 8, 10, 11, 12, 14, 16, 18, 19, 21	XXX	Carbendazim#, Diuron#, DEET, Diazinon§, Cybutryn, Tebuconazol#
Schwebstoffe - limnisch		X	QAV, Triclosan und TP Methyl-

Matrix	Relevante Produktarten	Relevant gemäß Monitoring-Daten	Beispiele nachgewiesener Stoffe/ Konzentrationsdaten › BG
			triclosan
Sedimente - limnisch		X	Cybutryn, Triclosan
Aquatische Organismen - limnisch		X	Triclosan und TP Methyltriclosan
Kläranlagenabläufe	PA 1, 2, 3, 4, 7, 10, 11, 12, 18, 19	X	Diuron#, Thiabendazol#, Triclosan und TP Methyltriclosan, Isoproturon#, Propiconazol#, Bromadiolon, Difenacoum#
Klärschlamm (relevant für indirekte Einträge in Böden)		X	BIT, Clorophene, Imazalil#, Cybutryn§
Boden (direkt)	PA 7, 8, 10, 14, 18, 19	-	-
Grundwasser		XX	Propiconazol#, Terbutryn
Terrestrische Organismen, ständig im Boden lebend (z.B. Regenwurm)		-	-
Terrestrische Organismen, teilweise auf dem Boden lebend/fressend, in der Nähe von Gebäuden/Bebauung (z.B. Nagetiere, Greifvögel)	PA 14	X	Difenacoum#, Bromadiolon# Coumatetralyl#, Brodifacoum#
Atmosphäre	PA 8, 11, 14, 18	-	Triclosan§
Gülle (relevant für indirekte Einträge in Böden)	PA 3, 18	-	-
Andere Matrices: Kompost, Gärgut	*	(X)	Imazalil#, Thiabendazol#, Tebuconazol#

zum Zeitpunkt der Untersuchung auch PSM-Wirkstoff; $ PA, die für indirekte Einträge über Kläranlagen relevant sind, siehe bei Kläranlagenabläufen; § aktuell keine Zulassung mehr für eine hier relevante PA; * Belastung vermutlich durch Rückstände von Pflanzenschutzmitteln.

Die vorliegenden Daten (Rüdel und Knopf 2012 und aktuelle Literaturauswertung in AP II deuten darauf hin, dass in Deutschland ein Biozidmonitoring bislang im Wesentlichen Oberflächengewässer (Wasserphase und Sedimente/Schwebstoffe), Kläranlagen-abläufe/ Klärschlamm und Grundwasser abdeckt. In anderen europäischen Untersuchungen spielen Untersuchungen von marinen Proben (Meerwasser und Sediment; für Antifouling-Wirkstoffe, PA 21) sowie Untersuchungen von Nagern und Greifvögeln auf Rodentizide (PA 14) eine größere Rolle (siehe auch Literaturauswertung in AP II).

Für Biota, Boden, Grundwasser und Gülle liegen nur wenige und für atmosphärische Belastungen nur vereinzelte Monitoring-Daten für Biozidwirkstoffe vor (zumindest für Deutschland, aus Skandinavien werden einzelne Untersuchungen berichtet, z.B. Nachweis von Triclosan in Luftproben). Hier sind weitere exemplarische Untersuchungen an potenziell belasteten Stellen erforderlich, um die mögliche Relevanz von Biozideinträgen in diese Kompartimente bzw. Umweltmedien bewerten zu können.

In den letzten Jahren gab es aus Großbritannien, Dänemark, Frankreich und Norwegen Hinweise auf Belastungen von Nagetieren und Räubern/Greifvögeln, die sich von diesen ernähren, mit Rodentiziden (Christensen et al. 2012; Hughes et al. 2013; Walker et al. 2012; siehe auch Workshop-Bericht, Jäger et al. 2013). Rückstände in Wildtieren stammen häufig von Antikoagulantien der 2. Generation, die für Produktart 14 in den Anhang I aufgenommen wurden (Rodentizide, Bekämpfung von Gesundheits-, Hygiene-, Vorrats- oder Materialschädlingen in und an Gebäuden, städtischen/industriellen Flächen und der Kanalisation).

Beim Einsatz von Rodentiziden in der Kanalisation können auch direkte Einträge in Gewässer durch Regenwassereinleitung bzw. über Regenwasserüberläufe erfolgen (Kahle und Nöh 2009; Gómez-Canela et al. 2014). Da einige Antikoagulantien der 1. und 2. Generation sowohl die PBT- bzw. vPvB-Kriterien erfüllen als auch unakzeptable Risiken in Bezug auf Primär- und Sekundärvergiftungen aufweisen, wurden strenge Risikominderungsmaßnahmen für diese Anwendungen vorgeschrieben und die Aufnahme in den Anhang I erfolgte nur für einen verkürzten Zeitraum von 5 Jahren (z.B. für Difenacoum). Um in diesem Zeitraum mögliche Gefährdungen von Nagetieren und Greifvögeln durch Rodentizide zu erfassen, sollte hierfür ein geeignetes Monitoring vorgesehen werden.

2 Priorisierung von Bioziden für das Monitoring

2.1 Hintergrund

Auf Grundlage der recherchierten Monitoring-Daten und Abschätzungen der Eintragspfade sowie mit Hilfe weiterer dem Umweltbundesamt vorliegender Daten potenziell relevanter biozider Wirkstoffe wurde im Vorläuferprojekt ein erstes Konzept zur Priorisierung erarbeitet (Rüdel und Knopf 2012). Dabei wurde berücksichtigt, dass unterschiedliche Umweltkompartimente je nach Eintragspfad und Stoffeigenschaften unterschiedlich stark betroffen sein können.

Auch evtl. bei der Anwendung entstehende oder in der Umwelt gebildete persistente Transformationsprodukte (TP) werden als relevant betrachtet (d.h., die TP sind analog zu den Wirkstoffen zu bewerten). In den vom Umweltbundsamt zur Verfügung gestellten Assessment Reports (so genannte Doc I-Berichte) sind teilweise direkt Angaben zu den Eigenschaften persistenter Transformationsprodukte enthalten (insbesondere in den Fällen, in den das Transformationsprodukt der eigentliche Wirkstoff ist, z.B. Methylisothiocyanat im Fall von Dazomet und Metam-Natrium).

Im Rahmen dieses Vorhabens wird das im Vorläuferprojekt vorgeschlagene Verfahren überprüft und optimiert. Außerdem erfolgt eine Sensitivitätsanalyse. Die Datenbasis wurde ebenfalls verbreitert (inzwischen ca. 135 Wirkstoffe sowie ca. 70 Transformationsprodukte; die für die TP berichteten Daten sind aber teilweise sehr lückenhaft).

Generell wurden die Daten den zur Verfügung gestellten Doc I-Reports entnommen. Viele der Berichte sind bereits von der EU Kommission öffentlich verfügbar gemacht worden (für die Stoffe, für die bereits eine Entscheidung zur Aufnahme in Anhang I getroffen wurde; recherchierbar unter http://echa.europa.eu/information-on-chemicals/biocidal-active-substances). Die hier als relevant identifizierten Daten wurden in einer Excel-Datei kompiliert. Sofern gegenüber dem Vorläuferprojekt aktuellere Assessment Reports verfügbar waren, wurden die Daten überprüft und - soweit erforderlich - aktualisiert. In einzelnen Fällen wurden fehlende Daten für Wirkstoffe mittels QSAR-Methoden abgeschätzt.

Um die Schwierigkeit der Unterscheidung von Pflanzenschutzmittel- und Biozideinträgen zu umgehen, wurde der Vorschlag des Umweltbundesamts berücksichtigt, im ersten Schritt nur solche Substanzen für ein Monitoring vorzusehen, die nicht in anderen Bereichen, also z.B. nicht als Pflanzenschutzmittel, verwendet werden (Wieck et al. 2010) bzw. für die aufgrund des Eintragspfades eindeutig biozide Anwendungen die Ursache von Umweltexpositionen sind. Wirkstoffe, die auch als Pflanzenschutzmittel zugelassen sind, können in den Auswertetabellen herausgefiltert werden.

Eine generelle Nutzung der bisherigen Biozidfunde im Umweltmonitoring als Kriterium für die Priorisierung wird nicht als sinnvoll erachtet. Zum einen würden so Stoffe, die derzeit schon regelmäßig gemessen werden, stärker gewichtet, und weitere, möglicherweise relevante Stoffe, nicht beachtet. Zum anderen sind bzw. waren die häufig nachgewiesenen Biozidwirkstoffe auch Pflanzenschutzmittel-Wirkstoffe (und die Funde zu einem großen Teil vermutlich auf diese Verwendung zurückzuführen).

Von den Stoffen, die bereits im Monitoring (vorwiegend Binnen-Oberflächengewässer) untersucht werden und Positivfunde aufweisen, erscheinen aber Irgarol/Cybutryn, 1,2-Benzisothiazolin-3-on (BIT), 2-n-Octyl-4-isothiazolin-3-on (OIT), Clorophene, Dichlofluanid (seit 2003 kein PSM mehr), Terbutryn (seit 2002 kein PSM mehr) und Triclocarban (seit 2009 nicht mehr als Biozid verkehrsfähig) relevant, da diese über einen längeren Zeitraum nur als Biozidwirkstoff verwendet werden bzw. wurden. Irgarol/Cybutryn, Dichlofluanid und Tolylfluanid sind evtl. auch in marinen Wasser- und Sedimentproben relevant (Einsatz in PA 21).

2.2 Priorisierungsvorschlag

Das vorgeschlagene Konzept (Rüdel und Knopf 2012) gliedert sich in drei Schritte:

1) Abschätzung der Emissionsrelevanz von Biozidwirkstoffen;
2) Bewertung der Relevanz der ökotoxikologischen Wirkung von Biozidwirkstoffen;
3) Bewertung der Relevanz von Umweltkompartimenten für ein Umweltmonitoring von Biozidwirkstoffen (auf Basis der Nutzung für verschiedene PA und des Verteilungsverhaltens der Wirkstoffe)

Als Basis für die Priorisierung wurden relevante (und verfügbare) Eigenschaften von bzw. Informationen zu Biozidwirkstoffen identifiziert. Falls für einen Wirkstoff die Bildung stabiler TP bekannt ist, sind diese entsprechend zu bewerten. Für eine Reihe von TP sind auch entsprechende Daten in den zur Verfügung gestellten Assessment Reports aufgeführt.

Die Anwendung des vorgeschlagenen Biozidwirkstoff-Priorisierungskonzepts erfolgt mit den Stoffen, für die das UBA (teilweise noch vertrauliche) Doc I-Berichte zur Verfügung gestellt hat (ca. 200, aber teilweise mehrere Berichte für Wirkstoffe, die für mehrere PT genutzt werden). Gemäß den oben dargestellten Kriterien konzentrierte sich die Arbeit auf Wirkstoffe, die als „nicht leicht biologisch abbaubar“ klassifiziert wurden bzw. bei denen eine Angabe dazu fehlt (ca. 170 Stoffe inkl. TP). Für diese Stoffe wurden Datensätze mit relevanten Eigenschaften aus den Dossiers zusammengestellt. Es ist außerdem zu beachten, dass aufgrund der Priorisierung der Produktarten für die Bewertung der Altwirkstoffe in der EU überdurchschnittlich viele Wirkstoffe in der Auswahl sind, die für Produkte der PA 8, 14 und 18 eingesetzt werden. Wirkstoffe, die aufgrund dieser Vorgehensweise aus PA geringerer Priorität stammen, beispielsweise Schutzmittel für Baumaterialien (PA 10) oder für Flüssigkeiten in Kühl- und Verfahrenssystemen (PA 11), sind im Testdatensatz in geringerer Zahl vorhanden, da die Bewertungen dieser Stoffe erst später abgeschlossen wurden bzw. werden.

Zudem ist eine Reihe von Stoffen enthalten, die nicht für ein Umweltmonitoring relevant erscheinen (z.B. 1-/2-Propanol, aktives Chlor, Natriumbromid, Siliciumdioxid, Natriumhypochlorit, Metallphosphide; hier wurden nur einige Basisdaten dieser Stoffe mit aufgenommen, um die Emissionsaspekte des Priorisierungsschemas im Hinblick auf diese Substanzen zu prüfen).

Wie im Vorläuferprojekt werden bei der Priorisierung im Wesentlichen organisch-chemische Biozide berücksichtigt. Nicht betrachtet wurden Stoffe wie DDT und Abbauprodukte, Lindan oder Pentachlorphenol („existierende“ Wirkstoffe nach Biozidrichtlinie, die aber nicht verkehrsfähig sind), da sie beim Umweltmonitoring als ubiquitäre Kontaminationen nachgewiesen werden, es aber keinen Zusammenhang zu aktuellen Biozidanwendungen gibt. Bestimmte natürlich vorkommende, leicht abbaubare bzw. abreagierende Stoffe (z.B. Milchsäure oder Formaldehyd) werden nicht erfasst. Auch anorganische Biozidwirkstoffe erscheinen für ein Umweltmonitoring weniger relevant, da es sich häufig um Stoffe handelt, die auch natürlich vorkommen oder auch aus anderen technischen/industriellen Prozessen in die Umwelt emittiert werden (ähnliche Ausschlüsse erfolgen beispielsweise beim Schweizer Priorisierungsvorgehen; I. Wittmer, Beitrag auf dem Biocides Monitoring Workshop, Berlin, November 2012; siehe Jäger et al. 2013). Somit könnten Monitoring-Ergebnisse für solche Stoffe nicht zweifelsfrei einer Quelle zugeordnet werden. Dies gilt beispielsweise für Salzsäure, Kohlendioxid oder Kupferverbindungen. Letztere kommen auch natürlich vor und sind für Lebewesen essenziell. Kupferemissionen können aus ehemaligen Bergbauregionen, industriellen Prozessen und aus der Anwendung als Pflanzenschutzmittel resultieren. Für Silber, das auch als Biozid verwendet wird, gibt es weitere unterschiedliche Nutzungen und der Anteil, den die Biozidanwendung hat, ist nicht abschätzbar. Als relevant angesehen werden im Rahmen des Projekts jedoch metallorganische Verbindungen (z.B. organische Zinnverbindungen, die allerdings nicht mehr zugelassen sind) und Metallkomplexe mit organischem Anteil (z.B. Zink- oder Kupferpyrithion, die relativ stabil und somit in der Umwelt zu erwarten sind).

Unter Berücksichtigung der schon vorhandenen Daten und den genannten Ausschlüssen wurden ca. 60 Assessment Reports neu ausgewertet (darunter aber nur ca. 20 bislang nicht berücksichtigte Wirkstoffe; damit sind Daten für ca. 100 nach den diskutierten Kriterien relevante Stoffe sowie für ca. 70 TP verfügbar).

Beispiele für Wirkstoffe, für die eine Aktualisierung der Daten erforderlich war, da eine neuere Version des Assessment Reports vorlag: Benzoesäure, Bifenthrin, Bromessigsäure, Deltamethrin, IPBC, Kreosot, Nonansäure, Perestan, Pyriproxyfen, Tebuconazol, Tolylfluanid, Thiamethoxam, verschiedene quaternäre Ammoniumverbindungen (z.B. BKC, ADBAC), Warfarin. Beispiele für Stoffe, für die bisher keine Assessment Reports vorlagen: Acetamiprid, 1,2-Benzisothiazolin-3(2H)-on, Cyphenothrin, Cyproconazol, Cyromazin, Didecyldimethylammoniumchlorid, Indoxacarb, Metofluthrin, 5-Chlor-2-(4-chlorphenoxy)phenol (DCPP), Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammoniumchlorid, Hexaflumuron, Triclosan (im Vorläuferprojekt wurden für Triclosan und das Transformationsprodukt Methyltriclosan nur Literaturdaten verwendet, da zu dem Zeitpunkt noch kein Doc I-Bericht verfügbar war).

Die Priorisierung erfolgt in einer Excel-Datei, die die relevanten Stoffdaten enthält. Für jedes Kompartiment wird eine Selektion entsprechend der vorgeschlagenen Kriterien durchgeführt (Setzen von Filtern). Das Ranking erfolgt mit abnehmender Gesamtpunktzahl für das Produkt der Punktzahlen aus den ersten beiden Schritten und der Punktzahl für die Relevanz für das entsprechende Kompartiment (auf Basis des Einsatzes in bestimmten PA (siehe Kapitel 2.5).

Es ist zu beachten, dass die hier generierten Listen nur einen ersten Empfehlungscharakter haben und nicht 1:1 in ein Monitoring umzusetzen sind. Vor der Umsetzung in ein praktisches Monitoring sind weitere Aspekte zu berücksichtigen. Beispielsweise sollten gegebenenfalls Hinweise, dass Stoffe nicht oder nur in geringem Maße eingesetzt werden, berücksichtigt werden. Die Emissionsrelevanz kann hier nicht auf Basis von tatsächlich in Deutschland eingesetzten Mengen bewertet werden, da die Daten bislang nicht zur Verfügung stehen. Hinzu kommen mögliche Einträge aus anderen Quellen außer der Biozidnutzung (z.B. für Stoffe, die auch als Pflanzenschutzmittel oder Arzneimittel verwendet werden), für die zu klären ist, ob sie die spätere Interpretation der Ergebnisse beeinträchtigen können. Zudem können auch analytische Aspekte eine Rolle spielen (Bestimmungsgrenzen, insbesondere für Stoffe mit hoher Wirkstärke, die nur in geringen Mengen eingesetzt werden). Bevor ein Stoff für ein Umweltmonitoring berücksichtigt wird, sollten solche Aspekte gründlich betrachtet werden (siehe auch AP IV).

2.3 Abschätzung der Emissionsrelevanz

Als erster Schritt erfolgt eine Abschätzung der Emissionsrelevanz. Dazu werden auf Basis des Vorschlags aus dem Vorläuferprojekt die folgenden zur Verfügung stehenden Daten verwendet:

Emissionsrelevante Produktart: PA 1, 2, 3, 4, 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 (siehe Kapitel 1); je PA 1 Punkt (maximal 3 Punkte; im Vergleich zum Vorläuferprojekt verringert von 5 auf 3, um die Gewichtung zu reduzieren).

Begründung: Bei Anwendung und Gebrauch von Biozidprodukten können Umwelteinträge erfolgen. Die Nutzung in unterschiedlichen Produktarten wird als ein Maß für den Gesamtverbrauch eines Wirkstoffes und damit der Höhe möglicher Umwelteinträge verwendet. In Ermangelung konkret verwertbarer Verbrauchsmengen pro Wirkstoff erfolgt bei der hier vorgeschlagenen Priorisierung die Abschätzung der Relevanz möglicher Emissionen über die Nutzung in emissionsrelevanten PA (direkte und indirekte Umwelteinträge; auf Basis der Studie von COWI 2009). In diesem Schritt erfolgt keine medienbezogene Emissionsbewertung der PA (siehe Schritt 3). Außerdem bleibt die Anzahl der verschiedenen Anwendungsszenarien innerhalb einer PA unberücksichtigt. Im Falle der zu bewertenden persistenten TP wurden für diese die PA-Angaben der Ausgangssubstanz verwendet.

Anzahl Produkte mit dem Wirkstoff im BAuA-Melderegister: bis zu 10 Produkte: 0 Punkte; 11 - 100 Produkte: 1 Punkt; 101 - 1000 Produkte: 2 Punkte; > 1000 Produkte: 3 Punkte (Stand Januar 2014).

Begründung: Die Anzahl der gemeldeten Produkte lässt keine Aussage über Produktionsmengen einzelner Wirkstoffe zu. Allerdings kann sie als Maß für den Gesamtverbrauch eines Wirkstoffes verwendet werden. Eine große Anzahl an Produkten lässt eine dispersive Verbreitung erwarten. Im Falle der zu bewertenden persistenten TP wurden für diese die BAuA-Angaben der Ausgangssubstanz verwendet.

Produktions- bzw. Importmengen (ESIS-Datenbank, http://esis.jrc.ec.europa.eu): < 10 t/a: 0 Punkte; 10 - 1000 t/a (low production volume chemical, LPVC): 2 Punkte; > 1000 t/a (high production volume chemical, HPVC): 3 Punkte; Default-Wert (falls Stoff nicht gelistet oder unklare Angabe zur Produktions-/Importmenge): 1 Punkt.

Begründung: Die Produktions- bzw. Importmenge eines Stoffes dient als erste Näherung für die Anwendungshäufigkeit und damit für potenzielle Umwelteinträge (und somit auch der Nachweismöglichkeit in Umweltmedien). Die Wirkstärke eines Stoffes wird in diesem Schritt nicht berücksichtigt. Die über ESIS ermittelte Größenordnung der Produktions- bzw. Importmenge eines Stoffes bezieht sich allerdings nicht allein auf den Biozideinsatz, sondern auf alle Nutzungen. Da diese aber auch teilweise zu Umwelteinträgen führen können, erscheint dieser Parameter trotzdem hier als Deskriptor geeignet. Im Falle der zu bewertenden persistenten TP wurden für diese die ESIS-Angaben der Ausgangssubstanz verwendet (falls der Metabolit ebenfalls in ESIS gelistet ist, ist gegebenenfalls die entsprechende höhere Einstufung zu verwenden).

Außerdem wird im Unterschied zum Vorläuferprojekt die Verwendung als Pflanzenschutzmittel (PSM) und in Veterinär- bzw. Humanarzneimitteln (AZM) nicht mehr im Rahmen der Emissionsrelevanz bewertet. Begründung: Da es ja um die Bewertung der Einträge aus der Biozidanwendung geht, könnten die Punktzahlen aus diesen Nutzungen das Ranking verfälschen. Die Angaben zur Zulassung als PSM bzw. Nutzung in AZM werden aber weiterhin erfasst (Daten aus Internetpublikationen des BVL für PSM; für AZM Abfrage über den Stoffnamen in der DIMDI-Datenbank AMIS - öffentlicher Teil; im Falle der zu bewertenden relevanten TP werden für diese die Angaben der Ausgangssubstanz verwendet). In den Ergebnistabellen der zur Auswertung verwendeten Excel-Datei wird dann jeweils aufgeführt, ob die Stoffe auch als PSM oder AZM verwendet werden bzw. wurden. Damit kann im Einzelfall bewertet werden, ob diese Nutzungen als zusätzliche Emissionsquellen zu berücksichtigen sind. In den meisten Tabellen sind aber aktuell auch als PSM genutzte Biozidwirkstoffe ausgefiltert (da das Monitoring zunächst auf nur als Biozide eingesetzte Stoffe beschränkt werden soll, um mögliche Interpretationsprobleme hinsichtlich der Ursache von Rückständen zu vermeiden; s.o.).

2.4 Bewertung der Relevanz von ökotoxikologischer Wirkung und Bioakkumulation

Im zweiten Schritt erfolgt die Bewertung der Relevanz von ökotoxikologischer Wirkung und Bioakkumulation. Für die Bewertung der ökotoxikologischen Relevanz wird hier primär die PNEC Wasser verwendet, da diese - im Gegensatz zur PNEC Boden - für die meisten Wirkstoffe in den Doc I-Berichten verfügbar ist. Zur PNEC Boden liegen nur für ca. 30 % der hier betrachteten Stoffe Angaben in den Doc I-Berichten vor. Wenn Daten zur ökotoxikologischen Wirkung von Biozidwirkstoffen auf Bodenorganismen aufgeführt werden, sind diese in einer Reihe der in diesem Projekt ausgewerteten Doc I-Berichten auf Basis der aquatischen Ökotoxizität abgeschätzt worden („equilibrium partitioning approach“; Berechnung auf Basis der unter Gleichgewichtsbedingungen in der Bodenlösung vorliegenden Stoffkonzentration unter Annahme einer ähnlichen Empfindlichkeit aquatischer und terrestrischer Organismen gegenüber dem Wirkstoff).

Da in diesem Schritt keine kompartimentspezifische Betrachtung erfolgt, erscheint das pragmatische Vorgehen, nur die breit verfügbaren Daten zur aquatischen Ökotoxizität zu nutzen, als akzeptabel.

Zur Bewertung der Relevanz von ökotoxikologischer Wirkung und Bioakkumulation werden die folgenden Daten aus den Doc I-Berichten verwendet (Nutzung von Daten, die in fast allen Berichten verfügbar sind):

PNEC Wasser: PNECs für aquatische Organismen werden wie folgt klassifiziert:

PNEC < 0,01 µg/L: 4 Punkte; 0,01 - 0,1 µg/L: 3 Punkte; > 0,1 - 1 µg/L: 2 Punkte; > 1 - 10 µg/L: 1 Punkt; > 10 µg/L: 0 Punkte. Wenn keine Daten angegeben sind (z.B. bei Transformationsprodukten) wird ein Default-Wert verwendet (1 Punkt).

Begründung: Die PNEC ermöglicht die Einschätzung der aquatischen Toxizität. Je nach Anzahl bzw. Art der verfügbaren Tests wird die PNEC durch Division der Wirkkonzentration für die empfindlichste Spezies durch bestimmte Assessment-Faktoren (AF) berechnet. In den meisten Fällen sind die PNEC-Werte in den Doc I-Berichten abgeleitet. Falls nicht, wurde die PNEC aus NOEC-Werten von Langzeittests (AF 100) bzw. LC50/EC50-Werten akuter Tests (AF 1000) berechnet.

PEC/PNEC-Vergleich im Dossier: PEC/PNEC > 1 für mehr als ein Szenario: 2 Punkte; PEC/PNEC > 1 für ein Szenario: 1 Punkt; PEC/PNEC für alle Szenarien < 1: 0 Punkte; keine Daten: Default-Wert = 1 Punkt.

Begründung: In den Stoff-Dossiers werden relevante Anwendungsszenarien bewertet. Diese Information wird hier verwendet. Die Szenarien beziehen sich aber auf Belastungen in der unmittelbaren Umgebung der Anwendung und die dafür abgeleiteten PEC-Werte sind nicht direkt auf Umweltmedien zu übertragen. In diesem Schritt erfolgt noch keine Differenzierung nach Kompartimenten (diese wird erst in Schritt 3 durchgeführt, siehe Kapitel 2.5).

T-Klassifizierung nach CLP: T+: 3 Punkte; T: 2 Punkte; weder T+ noch T: 0 Punkte;

Default-Wert: 1 Punkt.

Begründung: Das T-Kriterium berücksichtigt neben der Ökotoxizität auch eine mögliche Säugetiertoxizität.

Bioakkumulation im Fisch: Biokonzentrationsfaktor (BCF) < 100: 0 Punkte;
BCF > 100 - 2000: 1 Punkt; BCF > 2000: 2 Punkte; BCF > 5000: 3 Punkte.

Begründung: Die Bioakkumulation in Organismen kann zu einer Belastung in der Nahrungskette führen („secondary poisoning"). Bei fehlenden Werten für Wirkstoffe im Doc I-Bericht wurden Ergebnisse von QSAR-Abschätzungen ergänzt (EPI Suite, EPA 2007).

Der BCF für Regenwürmer wird nicht berücksichtigt, da die Datenbasis zu gering ist (nur in wenigen Doc I-Berichten Angaben dazu).

2.5 Bewertung der Relevanz von Umweltkompartimente für ein Monitoring

In diesem Schritt wird geprüft, in welchen Umweltkompartimenten (z.B. Wasserphase, Feststoff, Biota) ein Monitoring für die betrachteten Biozidwirkstoffe erfolgen sollte. Dabei wird einerseits die Emissionsrelevanz der einzelnen PA berücksichtigt (Emission in das betrachtete Kompartiment relevant?; dieser Aspekt wurde bereits in Kapitel 1 behandelt). Zum anderen wird das Verteilungsverhalten der Stoffe auf Basis der physikalisch-chemischen und sonstigen Eigenschaften (Koc, BCF, Persistenz) betrachtet (Vorkommen im betrachteten Kompartiment wahrscheinlich?).

In Abhängigkeit von der PA sind unterschiedliche Umweltkompartimente von möglichen Umwelteinträgen bei Anwendung oder Gebrauch von Bioziden betroffen (auf Grundlage von COWI 2009, ergänzt auf Basis der Expertise des UBA; siehe Kapitel 1; zu beachten: da für PA 15, 17 und 20 in Deutschland keine Zulassung vorgesehen ist, werden diese PA im Folgenden nicht berücksichtigt):

Oberflächengewässer für Produkte in PA 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 (zusätzlich indirekte Einträge über Kläranlagenabläufe; s.u.);

Böden für Produkte in PA 7, 8, 10, 14, 18, 19 (zusätzlich indirekte Einträge über Klärschlamm, s.u., und Gülle: PA 3, 18; siehe Kapitel 1);

Atmosphäre für Produkte in PA 8, 11, 14, 18 (zusätzliche indirekte Einträge über Verflüchtigung aus Boden und Wasser werden nicht berücksichtigt);

Kläranlagen (Schlamm und Ablauf): PA 1, 2, 3, 4, 7, 10, 11, 12, 18 19.

Je notifizierter PA wird 1 Punkt zugeordnet (maximal 3 Punkte; reduziert im Vergleich zum Vorläuferprojekt, damit der Maximalwert der Ergebnisse aller drei Schritte jeweils ähnlich hoch ist; d.h. 1 PA = 1 Punkt, 2 PA = 2 Punkte, ab 3 PA = 3 Punkte). Der Wert des Gesamtprodukts aus den ersten beiden Schritten (Emission und Effekte) und diesem Schritt wird zur Priorisierung innerhalb der relevanten Stoffe für das jeweilige Kompartiment verwendet.

Die weitere Bewertung hinsichtlich der Verteilung der betrachteten Biozidwirkstoffe in den relevanten Umweltkompartimenten wird in Kapitel 2.7 diskutiert.

2.6 Optimierung der Aggregation der Ergebnisse der Bewertungsschritte

Zunächst wurden die im Vorprojekt entwickelten Priorisierungskriterien mit dem aktualisierten Datensatz (zusätzliche Stoffe, teilweise aktualisierte Stoffdaten, Stand der Zulassung angepasst hinsichtlich Nichtzulassungsentscheidungen; Berücksichtigung aller relevanten PA) unverändert angewandt. Die Ergebnisse sind in den folgenden Tabellen im Vergleich dargestellt.

Es wird aber vorgeschlagen, die Aggregation der Ergebnisse für die Bewertung (d.h. für das Ranking) zu ändern. Statt der Addition der Punktzahlen aus den drei Schritten soll eine Multiplikation stattfinden.

Begründung: Zunächst wird eine stärkere Differenzierung der für die bewerteten Stoffe erzielten Punktsummen erreicht (größere Unterschiede im Ranking; bei beiden Vorgehensweisen bleibt der am höchsten gereihte Stoff gleich). Da die Relevanz für das Kompartiment (Schritt 3) auch teilweise mit 0 bewertet wird, erhalten die entsprechenden Stoffe einen Punktwert von 0 in der Multiplikation. Bei der Addition können solche Stoffe trotzdem relativ hoch gereiht werden, wenn sie hohe Emissions- und Wirkungsrelevanz haben. Zum anderen erscheint das im Multiplikationsansatz erhaltene Produkt aus Emissionsrelevanz und Wirkungsrelevanz aussagekräftiger als die Summe. In den folgenden Tabellen werden die Ergebnisse beider Vorgehensweisen verglichen.

Da aber zudem auch zusätzliche Stoffe bewertet werden können, wird zunächst ein Vergleich des alten Bewertungsansatzes (= Addition) auf Basis des Datenbestandes Ende 2011 (Tabelle 3; Rüdel und Knopf 2012) und Februar 2014 (Tabelle 4) durchgeführt. Es zeigt sich, dass der Anteil potentiell relevanter Wirkstoffe deutlich gestiegen ist, da nun eine Reihe von Stoffen enthalten ist, die für viele PA notifiziert wurden (z.B. quaternäre Ammoniumverbindungen) bzw. noch im Review-Programm sind. Auch für eine Reihe von Stoffen, die bereits in der Vorgängerliste enthalten waren, wurden nun alle PA für die Abschätzung der Expositionsrelevanz in den verschiedenen Medien berücksichtigt (im Vorprojekt waren nur die PA verwendet worden, für die Assessment Reports vorgelegt wurden; siehe z.B. DCOIT).

Tabelle 5 zeigt dann das Ergebnis, wenn statt der Addition eine Multiplikation zur Aggregation der Ergebnisse durchgeführt wird. Die am höchsten gereihten Stoffe unterscheiden sich nur wenig bei beiden Vorgehensweisen. Allerdings wird wie erwartet eine stärkere Differenzierung erreicht. Im unteren Bereich ändert sich die Reihenfolge etwas und statt Permethrin ist nun ein weiteres DCOIT-TP höher gereiht.

Tabelle 3: Priorisierung zum Monitoring in der Wasserphase (TOP 15, nur Biozide ohne PSM-Zulassung); unveränderte Priorisierungskriterien aus dem Vorprojekt; Stand Daten und Zulassungsentscheidungen Dezember 2011.

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Summe) Monitoring im Wasser
Methyltriclosan	4640-01-1	Keine	1,2,7,9	8	5	5	18
Triclosan	3380-34-5	Keine	1,2,7,9	8	4	5	17
Copper pyrithione	14915-37-8	Keine	21	4	10	2	16
Flufenoxuron	101463-69-8	Keine	8, 18	5	9	2	16
Hydrogen cyanide	74-90-8	2001	8, 14, 18	7	5	4	16
Difethialone	104653-34-1	2004	14	4	9	2	15
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	8, 21	6	6	3	15
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8	6	7	1	14
Dichlorvos	62-73-7	2007	18	5	8	1	14
Cyfluthrin	68359-37-5	2009	18	5	8	1	14
Flocoumafen	90035-08-8	2003	14	3	9	2	14
Creosote	8001-58-9	Keine	8	6	6	1	13
Dichlofluanid	1085-98-9	2003	8	6	6	1	13
Cybutryne (Irgarol)	28159-98-0	Keine	21	4	7	2	13
Didecylmethylpoly-(oxyethyl) ammonium propionate (Bardap 26)	94667-33-1	Keine	2, 4, 8	7	3	3	13

Tabelle 4: Priorisierung zum Monitoring in der Wasserphase (TOP 15, nur Biozide ohne PSM-Zulassung); unveränderte Priorisierungskriterien aus dem Vorprojekt; Stand Daten und Zulassungsentscheidungen Februar 2014.

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Summe) Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	7	9	6	22
Triclosan	3380-34-5	Keine	1,2,7,9	7	10	4	21
Alkyldimethylbenzyl-ammonium Chloride (ADBAC)	68424-85-1	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12, 13	8	6	6	20
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	8	7	5	20
N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (Lonzabac 12)	2372-82-9	Keine	2, 3, 4, 6, 8, 11, 12, 13	7	6	6	19
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	8	5	6	19
Didecyldimethyl ammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	8	5	6	19
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	7	8	4	19
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	7	5	6	18
Dichlofluanid	1085-98-9	2003	7, 8, 21	8	6	4	18
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	6	9	3	18

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Summe) Monitoring im Wasser
Didecylmethylpoly-(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	6	5	6	17
Tolylfluanid	731-27-1	2010	7, 8, 21	6	7	4	17
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	17
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	17

Tabelle 5: Priorisierung zum Monitoring in der Wasserphase (nur Biozide ohne PSM-Zulassung); aktualisierte Priorisierungskriterien, außerdem Multiplikation statt Summe für Gesamt-Score-Berechnung; Stand Daten und Zulassungsentscheidungen Februar 2014.

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	7	9	6	378
Alkyldimethylbenzyl-ammonium Chloride (ADBAC)	68424-85-1	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12, 13	8	6	6	288
Triclosan	3380-34-5	Keine	1,2,7,9	7	10	4	280
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	8	7	5	280
N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (Lonzabac 12)	2372-82-9	Keine	2, 3, 4, 6, 8, 11, 12, 13	7	6	6	252
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	8	5	6	240
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	8	5	6	240
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	7	8	4	224
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	7	5	6	210

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Dichlofluanid	1085-98-9	2003	7, 8, 21	8	6	4	192
Didecylmethylpoly(oxy-ethyl)ammonium Propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	6	5	6	180
Tolylfluanid	731-27-1	2010	7, 8, 21	6	7	4	168
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	168
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	168
NNOOA (DCOIT-TP EW) N-(n-octyl) oxamic acid	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	168

2.7 Optimierung des Priorisierungsansatzes und Ergebnisse des Rankings

In diesem Kapitel werden Optimierungen der Kriterien für das Ranking der Stoffe bezüglich des Biozidmonitoring in den verschiedenen Umweltmedien/Kompartimenten vorgeschlagen. Diese beziehen sich auf Schritt 3 des Priorisierungskonzepts (insbesondere auf die Berücksichtigung des Verteilungsverhaltens in den Umweltmedien). Die Beschreibung orientiert sich am Bericht zum Vorläuferprojekt (Rüdel und Knopf 2012).

2.7.1 Aquatisches Monitoring

Ein Monitoring in Oberflächengewässern wird empfohlen, wenn die Wirkstoffe direkt oder indirekt in Gewässer emittiert werden. Im ersten Schritt werden nicht nur persistente Stoffe berücksichtigt, da (z.B. über Kläranlagen) teilweise kontinuierlich emittierte abbaubare Stoffe als pseudo-persistent erscheinen (kontinuierliche Exposition, da Abbau und Neueintrag sich die Waage halten) und damit ebenfalls relevant sein können. Da im Testdatensatz vorwiegend „nicht leicht bioabbaubare“ Stoffe enthalten sind, sind potenziell pseudo-persistente Stoffe aber hier nur in geringer Anzahl berücksichtigt.

In Tabelle 6 sind die Ergebnisse des Ranking für ein Biozidmonitoring in der Wasserphase aufgeführt (TOP 20). Im Unterschied zu Tabelle 5 wurde ein zusätzlicher Filter verwendet, mit dem Wirkstoffe mit einem K_{OC} > 100000 herausgefiltert werden (diese sind beim Monitoring sinnvoller in Schwebstoffen zu erfassen). Würden auch Wirkstoffe berücksichtigt, die als PSM verwendet werden, würden auch Tebuconazol und Pyrethrine unter den TOP 20 aufgeführt (Platz 15 und 16, 140 bzw. 128 Punkte).

Gegebenenfalls kann es aber sinnvoll sein, leicht abbaubare Stoffe nicht in der Liste zu berücksichtigen und nur Stoffe mit einer gewissen Persistenz zu betrachten. Zur Differenzierung der Bewertung von Stoffen ohne Angaben und nicht leicht biologisch abbaubaren bzw. persistenten Stoffen wurde das Vorgehen gegenüber dem Vorläufervorhaben leicht verändert. In das hier verwendete Persistenzkriterium gehen ein:

- Angaben zur leichten biologischen Abbaubarkeit: leicht biologisch abbaubar: 0 Punkte; nicht leicht biologisch abbaubar: 2 Punkte; keine Angaben bzw. nicht anwendbar (z.B. bei anorganischen Metallverbindungen): 1 Punkt.
  Begründung: leicht abbaubare Stoffe wie Alkohole, anorganische Chlorverbindungen oder Fettsäuren erscheinen nicht relevant für ein Monitoring (soweit es keine Hinweise auf Pseudo-Persistenz gibt).
- Angaben zur Persistenz: P-Kriterium gemäß Biozidverordnung erfüllt: 2 Punkte, vP-Kriterium erfüllt: 3 Punkte; P-Kriterium nicht erfüllt: 0 Punkte; keine Angaben bzw. nicht anwendbar (z.B. bei anorganischen Metallverbindungen, da Metalle auch natürlich vorkommen): 1 Punkt.

Zur Berechnung des hier verwendeten Persistenzkriteriums wird die Summe gebildet aus den beiden Bewertungen für die leichte biologische Abbaubarkeit und die Persistenz. Stoffe mit 0 Punkten in diesem Schritt werden als nicht persistent angesehen und für die entsprechenden Auswertungen herausgefiltert.

Die Ergebnisse der entsprechenden Auswertung sind in Tabelle 7 dargestellt.

Tabelle 6: Priorisierung zum Monitoring in der Wasserphase (Top 20; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem K_{OC} < 100000.

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	7	9	6	378
Triclosan	3380-34-5	Keine	1,2,7,9	7	10	4	280
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	8	7	5	280
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	8	5	6	240
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	7	8	4	224
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	7	5	6	210
Dichlofluanid	1085-98-9	2003	7, 8, 21	8	6	4	192
Tolylfluanid	731-27-1	2010	7, 8, 21	6	7	4	168
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	168
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	168
NNOOA (DCOIT-TP EW) N-(n-octyl) oxamic acid	-	Keine	7, 8, 9, 10, 11, 21	7	4	6	168
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	6	9	3	162

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Hydrogen cyanide	74-90-8	2001	8, 14, 18	6	6	4	144
Decanoic acid	334-48-5	Keine	4, 18, 19	7	4	5	140
Methylisothiocyanate (MITC) (Dazomet TP)	556-61-6	2004	6, 8, 12	6	6	3	108
C(M)IT (5-chloro-2-methyl-4-isothiazolin-3-one)	26172-55-4	Keine	2, 4, 6, 11, 12, 13	7	3	5	105
PBC (Propargyl butyl carbamate) (IPBC TP)	76114-73-3	Keine	6, 7, 8, 9, 10, 12, 13	8	2	6	96
DMSA (Dichlofluanid TP)	4710-17-2	2003	7, 8, 21	8	3	4	96
Margosa extract (Aza-dirachtin A, B)	84696-25-3	Keine	18, 19	4	6	4	96
MIT (2-methyl-4-isothiazolin-3-one)	2682-20-4	Keine	2, 4, 6, 11, 12, 13	6	3	5	90

Tabelle 7: Priorisierung zum Monitoring in der Wasserphase (Top 20; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem K_{OC} < 100000, die nicht „readily biodegradable“ sind bzw. für die keine Information zur Abbaubarkeit vorliegt (Punktzahl Persistenz 0 bzw. 1).

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	2	7	9	6	378
Triclosan	3380-34-5	Keine	1,2,7,9	5	7	10	4	280
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	3	8	7	5	280
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	2	8	5	6	240
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	7	8	4	224
Dichlofluanid	1085-98-9	2003	7, 8, 21	3	8	6	4	192
Tolylfluanid	731-27-1	2010	7, 8, 21	2	6	7	4	168
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	3	7	4	6	168
NNOOA (DCOIT-TP EW) N-(n-octyl) oxamic acid	-	Keine	7, 8, 9, 10, 11, 21	2	7	4	6	168
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	3	162
Hydrogen cyanide	74-90-8	2001	8, 14, 18	2	6	6	4	144

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
methylisothiocyanate (MITC) (Dazomet TP)	556-61-6	2004	6, 8, 12	2	6	6	3	108
DMSA (Dichlofluanid TP)	4710-17-2	2003	7, 8, 21	3	8	3	4	96
PBC (Propargyl butyl carbamate) (IPBC TP)	76114-73-3	Keine	6, 7, 8, 9, 10, 12, 13	2	8	2	6	96
Margosa extract (Aza-dirachtin A, B)	84696-25-3	Keine	18, 19	2	4	6	4	96
MIT (2-methyl-4-isothiazolin-3-one)	2682-20-4	Keine	2, 4, 6, 11, 12, 13	3	6	3	5	90
DCPP (5-Chloro-2-(4-chlorophenoxy)-phenol)	3380-30-1	Keine	1, 2, 4	3	5	6	3	90
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	3	81
Thiabendazole	148-79-8	2011	7, 8, 9, 10	3	4	4	5	80
MIT (2-Methyl-2H-isothiazol-3-one)	2682-20-4	Keine	6. 11, 12, 13	3	5	4	4	80

Entsprechend der Leistungsbeschreibung sollte außerdem geprüft werden, ob das Ergebnis der in den Doc I-Berichten entsprechend den Anforderungen der Biozidverordnung (d.h. gemäß REACh Annex XIII) vorgenommenen Persistenzbewertungen kompartimentspezifisch verwendet werden kann. Dazu wurde - soweit Daten dazu in den Bewertungsberichten enthalten waren - jeweils identifiziert, ob die Stoffe in Wasser, Boden, oder Sediment persistent sind. Die so identifizierten relevanten persistenten Biozidwirkstoffe für das Monitoring in Oberflächengewässern sind in Tabelle 8 aufgelistet. Insgesamt sind nur wenige Stoffe als persistent klassifiziert (z.B. Chlorfenapyr oder Flocoumafen). Die aufgeführten persistenten oder potentiell persistenten Stoffe haben entsprechend der hier gewählten Kriterien auch nur eine geringe Relevanz für das Monitoring in der Wasserphase von Oberflächengewässern (geringerer Score im Vergleich zu Tabelle 7). Unter den am höchsten gereihten Stoffen sind einige Biozid-TP, für die keine P-Bewertung vorlag (Default = 1 Punkt bei der Persistenzbewertung). Nur die drei am höchsten gereihten Biozide aus Tabelle 8 (Permethrin, Margosa-Extrakt und Chlorfenapyr) waren auch in Tabelle 7 aufgeführt.

Es wird vorgeschlagen die Kriterien gemäß Tabelle 7 zu verwenden, da ansonsten die Gefahr besteht, relevante Stoffe auszuschließen (z.B. Triclosan, DCOIT, IPBC).

Tabelle 8: Priorisierung zum Monitoring in der Wasserphase (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem K_{OC} < 100000, die in Wasser als persistent bewertet werden (bzw. für die keine Bewertung angegeben wurde).

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (Wasser; aus Doc I-Bericht)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	insufficient data	6	9	3	162
Margosa extract (Azadirachtin A, B)	84696-25-3	Keine	18, 19	no data	4	6	4	96
Chlorfenapyr	122453-73-0	Keine	8, 18	yes	3	9	3	81
Methyl-DCPP (DCPP TP)	-	Keine	1, 2, 4	no data	5	5	3	75
3-Phenoxybenzyl alcohol (Permethrin TP W)	-	Keine	8, 9, 18	insufficient data	6	4	3	72
DCVA (Permethrin TP W) -(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropanecarboxylic acid	-	Keine	8, 9, 18	insufficient data	6	4	3	72
PBA (Permethrin TP W) 3-phenoxybenzoic acid	-	Keine	8, 9, 18	insufficient data	6	4	3	72
(AEM 5772 TP) 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	yes (expected)	3	5	3	45
Prallethrin	103065-19-6	Keine	18	no data	3	7	2	42

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (Wasser; aus Doc I-Bericht)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Creosote	8001-58-9	Keine	8	yes	5	8	1	40
Hexaflumuron	86479-06-3	Keine	18	no data	2	9	2	36
Flocoumafen	90035-08-8	2003	14	yes	3	10	1	30
Brodifacoum	56073-10-0	2010	14	potentially yes	3	9	1	27
CL 312094 (Chlorfenapyr TP)	-	Keine	8, 18	yes	3	3	3	27
AEM 5772 (Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride)	27668-52-6	Keine	2, 7, 9	yes (expected)	3	3	3	27
Icaridin acid (Icaridin TP)	-	Keine	19	no data	4	3	2	24
Bifenthrin	82657-04-3	2011	8	yes	2	9	1	18
Bromadiolone	28772-56-7	2011	14	yes	3	6	1	18
ethylene thiourea (ETU) (Zineb TP)	96-45-7	1997	21	potentially yes	5	3	1	15
EU (Zineb TP W,S)	-	1997	21	yes	5	3	1	15

Ein Monitoring in aquatischer Biota erscheint sinnvoll, wenn die Wirkstoffe direkt oder indirekt in Gewässer emittiert werden, persistent sind und einen Fisch-BCF > 100 auf-weisen (Kriterien wie im Vorläuferprojekt). Es wurden zwei Auswertungen durchgeführt, einmal mit den Persistenzkriterien aus dem Vorläuferprojekt und zusätzlich mit der kompartimentspezifischen Persistenz im Wasser als Filterkriterium (Tabelle 9 und Tabelle 10).

Im Vergleich erscheint das Ergebnis des ersten Bewertungsansatzes zur Persistenz relevanter (d.h. Berücksichtigung aller Stoffe, die nicht leicht abbaubar sind; Tabelle 9). Wird das strenge Persistenz-Kriterium angewandt, fallen Triclosan und Methyltriclosan heraus (Tabelle 10; diese Stoffe werden zwar im Doc I-Bericht vorläufig nicht als persistent bewertet, doch werden weitere Untersuchungen als notwendig erachtet). Da für diese Stoffe aber ein Potential zur Bioakkumulation in Fischen bekannt ist (z.B. Rüdel et al. 2013), erscheint das Kriterium Persistenz gemäß Biozidverordnung bzw. REACh Annex XIII als zu streng für diese Priorisierung.

Auf der Liste gemäß Tabelle 10 erscheinen mehrere Rodentizide (PA 14), für die ein Monitoring in Fischen im Rahmen des Vorhabens geplant ist (aufgrund der geringen Gesamt-Punktzahl nicht unter den TOP 15 in Tabelle 9).

Zusätzlich zur Bewertung der Persistenz wird geprüft, inwieweit das Risiko von Sekundärvergiftungen als Kriterium genutzt werden kann (Angaben meistens in Doc I-Berichten enthalten) und wie sich dadurch das Ranking ändert. Diese Auswertung (Tabelle 11) unterstützt die Begründung der Auswahl von Rodentizid-Wirkstoffen für das Monitoring in Fischen.

Tabelle 9: Priorisierung zum Monitoring in aquatischen Biota (TOP 15; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem BCF › 100, die nicht „readily biodegradable“ sind (Punktzahl Persistenz › 0).

Ranking AQUATISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	2	7	9	6	378
Triclosan	3380-34-5	Keine	1,2,7,9	5	7	10	4	280
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	7	8	4	224
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	3	162
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	3	81
Methyl-DCPP (DCPP TP)	0	Keine	1, 2, 4	4	5	5	3	75
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	3	8	2	48
Transfluthrin	118712-89-3	Keine	18	3	4	6	2	48

Ranking AQUATISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Flufenoxuron	101463-69-8	Keine	8	5	4	11	1	44
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	5	3	7	2	42
Prallethrin	103065-19-6	Keine	18	3	3	7	2	42
Creosote	8001-58-9	Keine	8	4	5	8	1	40
Cyfluthrin	68359-37-5	2009	18	4	2	10	2	40
Cybutryne (Irgarol)	28159-98-0	Keine	21	4	5	8	1	40
Fenoxycarb	72490-01-8	2013	8	2	4	9	1	36

Tabelle 10: Priorisierung zum Monitoring in aquatischen Biota (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem BCF › 100, die in Wasser als persistent bewertet werden (bzw. für die keine Bewertung angegeben wurde).

Ranking AQUATISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	insufficient data	6	9	3	162
Chlorfenapyr	122453-73-0	Keine	8, 18	yes	3	9	3	81
Methyl-DCPP (DCPP TP)	-	Keine	1, 2, 4	no data	5	5	3	75
Prallethrin	103065-19-6	Keine	18	no data	3	7	2	42
Creosote	8001-58-9	Keine	8	yes	5	8	1	40
Hexaflumuron	86479-06-3	Keine	18	no data	2	9	2	36
Flocoumafen	90035-08-8	2003	14	yes	3	10	1	30
Brodifacoum	56073-10-0	2010	14	potentially yes	3	9	1	27
CL 312094 (Chlorfenapyr TP)	-	Keine	8, 18	yes	3	3	3	27

Ranking AQUATISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Bifenthrin	82657-04-3	2011	8	yes	2	9	1	18
Bromadiolone	28772-56-7	2011	14	yes	3	6	1	18
Polymeric betaine	214710-34-6	Keine	8	no data	3	4	1	12

Tabelle 11: Priorisierung zum Monitoring in aquatischen Biota (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe, die nicht „readily biodegradable“ sind (Punktzahl Persistenz › 0), einen BCF › 100 haben und als relevant hinsichtlich „secondary poisoning“ in aquatischen Systemen bewertet werden.

Ranking AQUATISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Potenzial „secondary poisoning“	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Triclosan	3380-34-5	Keine	1,2,7,9	aquatisch	7	10	4	280
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	aquatisch, terrestrisch	6	9	3	162
Difethialone	104653-34-1	2004	14	aquatisch, terrestrisch	3	10	1	30
Brodifacoum	56073-10-0	2010	14	aquatisch, terrestrisch	3	9	1	27
S-Methoprene	65733-16-6	Keine	18	aquatisch, terrestrisch	3	4	2	24

Ein Monitoring von Sediment und Schwebstoffen wird empfohlen, wenn die Wirkstoffe direkt oder indirekt in Wasser emittiert werden und einen K_{OC} > 10000 aufweisen (vergl. auch Zuordnung von Stoffen für ein Schwebstoff- und Sedimentmonitoring bei Rüdel et al. 2007; bei Wirkstoffen Berechnung mittels EPI Suite, EPA 2007, falls kein Koc angegeben). Die Ergebnisse zeigt Tabelle 12. Oben in der Liste finden sich zwei QAV. Außerdem sind eine Reihe von Insektiziden und Rodentiziden in der Gruppe der selektierten Stoffe.

Auch hier wird zum Vergleich die Persistenz alternativ gemäß den EU-Kriterien für das Kompartiment Sediment bewertet (Tabelle 13). Die sich ergebenden Reihenfolgen bei beiden Bewertungsansätzen unterscheiden sich etwas. Beispielsweise fällt DDAC (TOP 1 in Tabelle 12), das als nicht „readily biodegradable" klassifiziert wird, in Tabelle 13 heraus, da es als nicht persistent bewertet wird. Das gleiche gilt z.B. auch für Transfluthrin und Flufenoxuron).

Triclosan und Methyltriclosan, die im Vorläuferprojekt hier ebenfalls priorisiert wurden, fallen heraus, da im nun vorliegenden Doc I-Bericht niedrigere experimentelle Verteilungskoeffizienten K_{OC} angegeben werden als der im Vorläuferprojekt recherchierte (Triclosan) bzw. mittels EPI-Suite abgeschätzte (Methyltriclosan).

Aus Konsistenzgründen wird vorgeschlagen die Kriterien gemäß Tabelle 12 zu verwenden (entsprechend dem Vorgehen für die Wasserphase).

Tabelle 12: Priorisierung zum Monitoring in Sediment und Schwebstoffen (TOP 15; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem K_{OC} › 10000, die nicht „readily biodegradable“ sind (Punktzahl Persistenz › 0).

Ranking SEDIMENT/ SCHWEBSTOFFE Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Didecyldimethyl ammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	5	6	240
Didecylmethyl-poly (oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	5	6	180
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	3	162
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	3	81
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	3	8	2	48
Transfluthrin	118712-89-3	Keine	18	3	4	6	2	48

Ranking SEDIMENT/ SCHWEBSTOFFE Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
(AEM 5772 TP) 3-(trihydroxysilyl) propyl-dimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	2	3	5	3	45
Flufenoxuron	101463-69-8	Keine	8	5	4	11	1	44
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	5	3	7	2	42
Creosote	8001-58-9	Keine	8	4	5	8	1	40
Cyfluthrin	68359-37-5	2009	18	4	2	10	2	40
Pyriproxyfen	95737-68-1	Keine	18	2	3	6	2	36
Hexaflumuron	86479-06-3	Keine	18	5	2	9	2	36
Triflumuron	64628-44-0	1998	18	2	4	4	2	32
Flocoumafen	90035-08-8	2003	14	5	3	10	1	30

Tabelle 13: Priorisierung zum Monitoring in Sediment und Schwebstoffen (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem K_{OC} › 10000, die im Sediment als persistent bewertet werden (bzw. für die keine Bewertung angegeben wurde).

Ranking SEDIMENT/ SCHWEBSTOFFE Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Didecylmethylpoly (oxy-ethyl) ammonium pro-pionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	yes	6	5	6	180
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	insufficient data	6	9	3	162
Chlorfenapyr	122453-73-0	Keine	8, 18	yes	3	9	3	81
(AEM 5772 TP) 3-(tri-hydroxysilyl) propyldi-methyloctadecyl ammo-nium chloride	199111-50-7	Keine	2, 7, 9	yes (ex-pected)	3	5	3	45
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	potentially yes	3	7	2	42
Creosote	8001-58-9	Keine	8	yes	5	8	1	40
Hexaflumuron	86479-06-3	Keine	18	no data	2	9	2	36
Flocoumafen	90035-	2003	14	yes	3	10	1	30

Ranking SEDIMENT/ SCHWEBSTOFFE Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
	08-8							
Difethialone	104653-34-1	2004	14	yes	3	10	1	30
Brodifacoum	56073-10-0	2010	14	potentially yes	3	9	1	27
AEM 5772 (Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride)	27668-52-6	keine	2, 7, 9	yes (expected)	3	3	3	27
Bifenthrin	82657-04-3	2011	8	yes	2	9	1	18
Polymeric betaine	214710-34-6	keine	8	no data	3	4	1	12
Cyphenothrin	39515-40-7	keine	18	no data	2	3	2	12
Chlorophacinone	3691-35-8	2010	14	yes	2	5	1	10

2.7.2 Terrestrisches Monitoring

Ein Monitoring von Böden wird empfohlen, wenn die Wirkstoffe direkt oder indirekt in Böden emittiert werden (d.h. bodenrelevante PA), nicht leicht bioabbaubar sind und einen $K_{OC} > 10000$ aufweisen (Tabelle 14).

Auch in diesem Fall wird zum Vergleich die Persistenz alternativ gemäß den EU-Kriterien für das Kompartiment Boden bewertet (Tabelle 15). Die Reihenfolge bei beiden Bewertungsansätzen unterscheidet sich. So fallen die in Tabelle 14 hoch gereihten Biozide DDAC, Chrysanthemum-Extrakt und Transfluthrin bei Berücksichtigung der Persistenz gemäß EU-Kriterien heraus. Da so die Gefahr besteht, relevante Stoffe auszuschließen sowie aus Konsistenzgründen wird vorgeschlagen die Kriterien gemäß Tabelle 14 zu verwenden (entsprechend dem Vorgehen für die Wasserphase).

Tabelle 14: Priorisierung zum Monitoring in Böden (TOP 15; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe, die nicht „readily biodegradable" sind (Punktzahl Persistenz › 0) und einen K_{OC} › 10000 haben.

Ranking BODEN Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	5	6	240
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	4	216
Didecylmethyl-poly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	5	5	150
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	4	108
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	3	8	3	72
Transfluthrin	118712-89-3	Keine	18	3	4	6	3	72
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	5	3	7	3	63

Ranking BODEN Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Cyfluthrin	68359-37-5	2009	18	4	2	10	3	60
Pyriproxyfen	95737-68-1	Keine	18	2	3	6	3	54
Hexaflumuron	86479-06-3	Keine	18	5	2	9	3	54
Triflumuron	64628-44-0	1998	18	2	4	4	3	48
(AEM 5772 TP) 3-(tri-hydroxysilyl) propyldi-methyloctadecyl ammo-nium chloride	199111-50-7	Keine	2, 7, 9	2	3	5	3	45
Flufenoxuron	101463-69-8	Keine	8	5	4	11	1	44

Tabelle 15: Priorisierung zum Monitoring in Böden (TOP 15; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit einem K_{OC} › 10000, die im Boden als „persistent“ bewertet werden (bzw. für die keine Bewertung angegeben wurde).

Ranking BODEN Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (im Boden)	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	yes	6	9	4	216
Didecylmethylpoly(oxy-ethyl)ammonium Propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	no data	6	5	5	150
Chlorfenapyr	122453-73-0	Keine	8, 18	yes	3	9	4	108
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	potentially yes	3	7	3	63
Cyfluthrin	68359-37-5	2009	18	yes	2	10	3	60
Hexaflumuron	86479-06-3	Keine	18	yes	2	9	3	54
(AEM 5772 TP) 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	no data	3	5	3	45

Ranking BODEN Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (im Boden)	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Flufenoxuron	101463-69-8	Keine	8	yes	4	11	1	44
Creosote	8001-58-9	Keine	8	yes	5	8	1	40
Flocoumafen	90035-08-8	2003	14	yes	3	10	1	30
Difethialone	104653-34-1	2004	14	yes	3	10	1	30
Brodifacoum	56073-10-0	2010	14	potentially yes	3	9	1	27
AEM 5772 (Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride)	27668-52-6	Keine	2, 7, 9	no data	3	3	3	27
Bifenthrin	82657-04-3	2011	8	yes	2	9	1	18
Cyphenothrin	39515-40-7	Keine	18	no data	2	3	3	18

Nach einem direkten bzw. indirekten Eintrag von Bioziden in den Boden (s.o.) kann es zu einem möglichen Austrag in das Grundwasser kommen. Der hier betrachtete Eintragspfad geht über den Boden. Biozidwirkstoffe, die in bodenrelevante PA eingesetzt werden, erscheinen als relevant für ein Grundwassermonitoring, da ein Teil der Grundwasserneubildung über das Niederschlagswasser erfolgt. Ein Aspekt, der derzeit in diesem Priorisierungskonzept nicht weiter betrachtet wird, ist, dass Grundwasser auch durch Oberflächenwasser gespeist werden kann. Oberflächengewässer (Flüsse oder Seen) sind entweder durch eine Bodenschicht, durch die das Wasser sickert vom Grundwasser getrennt, oder das Grundwasser wird direkt mit Oberflächenwasser angereichert, da das Oberflächengewässer im Grundwasserleiter liegt. Bei diesem Eintragspfad müssten auch Biozidwirkstoffe, die in oberflächenwasserrelevanten PA eingesetzt werden, betrachtet werden.

Zur Beurteilung eines möglichen Eintrags aus dem Boden in das Grundwasser wird die Mobilität im Boden betrachtet (als intrinsische Stoffeigenschaft unabhängig von Bodeneigenschaften, berechnet als „Groundwater Ubiquity Score“, GUS, nach Gustafson 1989):
GUS > 2,8 = hohe Mobilität; GUS > 1,8 < 2,8 = mittlere Mobilität; GUS < 1,8 = niedrige Mobilität.

Begründung: die Mobilität im Boden ist ein wichtiges Kriterium hinsichtlich einer möglichen Grundwassergefährdung. Der GUS wird wie folgt berechnet (Gustafson 1989):
GUS = log(DT50) × (4 - log(K_{OC})).
Fehlende K_{OC}-Werte für Wirkstoffe werden berechnet (EPI-Suite, EPA 2007).

Ein Monitoring von Grundwasser sollte geprüft werden, wenn die Wirkstoffe direkt oder indirekt in Böden emittiert werden und einen GUS > 2,8 aufweisen. Der GUS war allerdings nicht für alle Wirkstoffe bzw. TP berechenbar, da Angaben zum Bodenabbau im Testdatensatz oft fehlen. Die Liste ist in Tabelle 16 dargestellt.

Über die DT50 für den Bodenabbau, die in die GUS-Berechnung eingeht, ist darin auch ein Persistenzkriterium abgedeckt. Wird die Persistenz zusätzlich bewertet, fallen Stoffe heraus. Werden nur Stoffe berücksichtigt, die nicht „readily biodegradable“ sind, fallen Warfarin und Natrium-Warfarin heraus (beide Biozide werden als „readily biodegradable“ eingestuft). Werden die EU-Persistenzkriterien für Boden angewandt, bleiben nur Fipronil und Permethric acid (Cyfluthrin TP) übrig (alle anderen Stoffe erfüllen die Persistenzkriterien nicht).

Um darzustellen, welche Stoffe derzeit mangels K_{OC}/DT50-Daten nicht bewertet werden, wird zusätzlich folgendermaßen vorgegangen: Zuordnung eines GUS Default-Wertes von 3.0 für alle Stoffe, für die K_{OC}/DT50-Daten fehlen; Berücksichtigung aller Stoffe, die nicht „readily biodegradable“ sind (Tabelle 17). Bei diesem Vorgehen werden beispielsweise DDAC, Blausäure, Decansäure und BIT sowie vorwiegend Transformationsprodukte von Biozidwirkstoffen selektiert.

Tabelle 16: Priorisierung zum Monitoring in Grundwasser (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe mit GUS › 2,8.

Ranking GRUNDWASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	GUS	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
DMSA (Dichlofluanid TP)	4710-17-2	2003	7, 8, 21	4,3	8	3	3	72
Methylisothiocyanate (MITC) (Dazomet TP)	556-61-6	2004	6, 8, 12	3,7	6	6	2	72
C(M)IT (5-chloro-2-methyl-4-isothiazolin-3-one)	26172-55-4	Keine	2, 4, 6, 11, 12, 13	3,4	7	3	3	63
Fipronil	120068-37-3	Keine	18	2,9	3	6	3	54
MIT (2-methyl-4-isothiazolin-3-one)	2682-20-4	Keine	2, 4, 6, 11, 12, 13	4,7	6	3	3	54
FPB-acid (Cyfluthrin TP W,S)	-	2009	18	4,0	2	4	3	24
Sodium Warfarin	129-06-6	1974	14	3,3	2	4	2	16
Permethric acid (Cyfluthrin TP W,S)	-	2009	18	4,2	2	2	3	12
Warfarin	81-81-2	2012	14	3,3	2	4	1	8

Tabelle 17: Priorisierung zum Monitoring in Grundwasser (TOP 15; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe, die nicht „readily biodegradable“ sind mit GUS › 2,8 (Default-Wert *3,0* für alle Stoffe, für die mangels Daten kein GUS berechnet werden kann).

Ranking GRUNDWASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	GUS	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	*3,0*	8	5	6	240
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	*3,0*	7	5	6	210
Hydrogen cyanide	74-90-8	2001	8, 14, 18	*3,0*	6	6	5	180
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	Keine	7, 8, 9, 10, 11, 21	*3,0*	7	4	6	168
(DCOIT-TP) 2-chloro-2-(n-octyl-carbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	*3,0*	7	4	6	168
Decanoic acid	334-48-5	Keine	4, 18, 19	*3,0*	7	4	6	168
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	*3,0*	8	7	3	168
Didecylmethyl-poly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	*3,0*	6	5	5	150
Octanoic acid	124-07-2	Keine	4, 18	*3,0*	6	4	4	96

Ranking GRUNDWASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	GUS	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Methyl-DCPP (DCPP TP)	-	Keine	1, 2, 4	*3,0*	5	5	3	75
DMSA (Dichlofluanid TP)	4710-17-2	2003	7, 8, 21	4,3	8	3	3	72
Transfluthrin	118712-89-3	Keine	18	*3,0*	4	6	3	72
Methylisothiocyanate (MITC) (Dazomet TP)	556-61-6	2004	6, 8, 12	3,7	6	6	2	72
C(M)IT (5-chloro-2-methyl-4-isothiazolin-3-one)	26172-55-4	Keine	2, 4, 6, 11, 12, 13	3,4	7	3	3	63
Prallethrin	103065-19-6	Keine	18	*3,0*	3	7	3	63

Alternativ könnte das System von McCall et al. (1981) zur Klassifizierung von Stoffen hinsichtlich der Mobilität im Boden auf Basis des Adsorptionskoeffizienten verwendet werden. Damit würde die Notwendigkeit der Verfügbarkeit von Daten zum Bodenabbau entfallen. Die Bewertung auf Basis des K_{OC} erfolgt hier wie folgend: immobil (K_{OC} > 5000) = 0 Punkte; geringe Mobilität (K_{OC} 5000 - > 2000) = 1 Punkt; niedrige Mobilität (K_{OC} 2000 - > 500) = 2 Punkte; mäßige Mobilität (K_{OC} 500 - > 150) = 3 Punkte; hohe Mobilität (K_{OC} 150 - > 50) = 4 Punkte; sehr hohe Mobilität (K_{OC} 50 - 0) = 5 Punkte. Als Default-Wert bei fehlendem K_{OC} wird eine mäßige Mobilität angenommen (= 3 Punkte).

Das Resultat der Priorisierung für das Monitoring von Grundwasser unter Berücksichtigung der Bewertung der Mobilität im Boden auf Basis des K_{OC} (McCall et al. 1981) ist in Tabelle 18 dargestellt. Selektiert wurden die Stoffe mit dem höchsten McCall-Wert (= 5; entspricht einem K_{OC} < 50). Bei diesem Vorgehen werden MITC (Dazomet TP), Bendiocarb und MIT am höchsten gereiht. Viele der so selektierten Stoffe sind aber wenig persistent, so dass nicht zu erwarten ist, dass sie ins Grundwasser versickern. Deshalb erscheint es notwendig, den McCall-Wert mit einem Persistenz-Kriterium zu verknüpfen.

Wenn Stoffe mit McCall-Werten von 4 und 5 selektiert und zusätzlich hinsichtlich der Persistenz bewertet werden (Persistenz-Punkteanzahl > 1), ergibt sich die in Tabelle 19 gezeigte Reihung. Bei diesem Vorgehen erhalten IPBC, BIT und Margosa-Extrakt die höchsten Punktzahlen.

Da die McCall-Bewertung hier nur in Kombination mit der Persistenz angemessen einsetzbar erscheint, wird vorgeschlagen, die Kriterien auf Basis des GUS gemäß Tabelle 16 zu verwenden (d.h., den GUS zu verwenden, allerdings ohne Default-Werte). Der GUS ist ein etablierter Wert, der Mobilitäts- und Persistenz-Eigenschaften integriert. Die Datenlage ist bei beiden Vorgehen nicht optimal, da die Informationen zur Persistenz (bzw. zum Bodenabbau) häufig fehlen.

Tabelle 18: Priorisierung zum Monitoring in Grundwasser (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Zur Beurteilung der Bodenmobilität wird das System nach McCall et al. (1981) angewandt; hier wurden die Stoffe mit dem höchsten McCall-Wert (= 5) selektiert.

Ranking GRUNDWASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	McCall K_{OC} Score	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Boden-relevanz	SCORE (Produkt) Monitoring terrestrisch
Methylisothiocyanate (MITC) (Dazomet TP)	556-61-6	2004	6, 8, 12	5	2	6	6	2	72
Bendiocarb	22781-23-3	2003	18	5	2	4	5	3	60
MIT (2-methyl-4-isothiazolin-3-one)	2682-20-4	Keine	2, 4, 6, 11, 12, 13	5	3	6	3	3	54
Cyanamide	420-04-2	2001	3, 18	5	3	5	2	5	50
Bromochlorodimethyl-hydantoin	32718-18-6	Keine	2, 11, 12	5	0	7	2	3	42
MIT (2-Methyl-2H-isothiazol-3-one)	2682-20-4	Keine	6. 11, 12, 13	5	3	5	4	2	40
PYPAC (Pyriproxyfen TP)	-	Keine	18	5	2	3	4	3	36
Lactic acid	79-33-4	Keine	2, 3, 4, 6	5	1	8	1	3	24
N'N-DMS (Tolylfluanid TP)	3984-14-3	2010	7, 8, 21	5	1	6	1	3	18
Potassium sorbate	24634-61-5	Keine	6, 8	5	0	5	1	1	5

Ranking GRUNDWASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	McCall K_{OC} Score	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Boden-relevanz	SCORE (Produkt) Monitoring terrestrisch
Bromoacetic acid (MBAA)	79-08-3	Keine	4	5	0	4	1	1	4
Perestane	847871-03-8	Keine	2	5	1	2	2	1	4
Magnesium-mono-peroxyphthalate-hexa-hydrate (MMPP)	84665-66-7	Keine	2	5	0	2	1	1	2

Tabelle 19: Priorisierung zum Monitoring in Grundwasser (alle; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Zur Beurteilung der Bodenmobilität wird das System nach McCall et al. (1981) angewandt; hier wurden die Stoffe mit McCall-Werten von 4 und 5 sowie mit einem Persistenz-Wert von › 1 selektiert.

Ranking GRUNDWASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	McCall Koc Score	Per-sistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Bodenrele-vanz	SCORE (Produkt) Monitoring terrestrisch
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	4	2	8	5	6	240
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	4	3	8	7	3	168
Margosa extract (Azadi-rachtin A, B)	84696-25-3	Keine	18, 19	4	2	4	6	5	120
N,N-Dimethyl-N'-phenyl-sulfamide (DMSA) (Dich-lofluanid TP)	4710-17-2	2003	7, 8, 21	4	3	8	3	3	72
Methylisothiocyanate (MITC) (Dazomet TP)	556-61-6	2004	6, 8, 12	5	2	6	6	2	72
Bendiocarb	22781-23-3	2003	18	5	2	4	5	3	60
MIT (2-methyl-4-isothiazolin-3-one)	2682-20-4	Keine	2, 4, 6, 11, 12, 13	5	3	6	3	3	54
Cyanamide	420-04-2	2001	3, 18	5	3	5	2	5	50
Naled	300-76-5	1976	(18)	4	2	3	5	3	45

Ranking GRUNDWASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	McCall K_{OC} Score	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
MIT (2-Methyl-2H-isothiazol-3-one)	2682-20-4	Keine	6. 11, 12, 13	5	3	5	4	2	40
PYPAC (Pyriproxyfen TP)	-	Keine	18	5	2	3	4	3	36
FPB-acid (Cyfluthrin TP W,S)	-	2009	18	4	2	2	4	3	24
DMST (Tolylfluanid TP)	66840-71-9	2010	7, 8, 21	4	3	6	1	3	18
Permethric acid (Cyfluthrin TP W,S)	-	2009	18	4	4	2	2	3	12
Alphachloralose	15879-93-3	1976	14	4	5	2	5	1	10

Ein Monitoring in terrestrischer Biota sollte geprüft werden, wenn die Wirkstoffe direkt oder indirekt in Böden emittiert werden und einen BCF > 2000 aufweisen (verwendet wird der BCF für Fisch, da nur in wenigen Fällen ein BCF für Regenwurm angegeben wird; es wird hier ein höherer BCF-Schwellenwert von 2000 verwendet statt 100 wie bei aquatischen Biota, s.o.). Die Ergebnisse sind in Tabelle 20 zusammengestellt.

Auch hier wird zum Vergleich die Bewertung der Persistenz entsprechend der EU-Kriterien (REACh Annex XIII) für das Kompartiment Boden berücksichtigt (Tabelle 21). Die generierten Stofflisten unterscheiden sich bei beiden Vorgehensweisen nicht. Aus Konsistenzgründen wird deshalb vorgeschlagen, die Kriterien gemäß Tabelle 20 zu verwenden.

Als weiterer Aspekt kann auch das Risiko von Sekundärvergiftungen in terrestrischer Biota bewertet werden. Für folgende drei Stoffe der Listen sind in den Doc I-Berichten Angaben zur Relevanz von Sekundärvergiftungen aufgeführt: Flocoumafen, Difethialon, Brodifacoum.

Tabelle 20: Priorisierung zum Monitoring in terrestrischer Biota (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe, die nicht „readily biodegradable“ sind (Punktzahl Persistenz › 0) und einen BCF(Fisch) › 2000 haben.

Ranking TERRESTRISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Boden-relevanz	SCORE (Produkt) Monitoring terrestrisch
Triclosan	3380-34-5	Keine	1,2,7,9	5	7	10	4	280
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	7	8	4	224
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	4	108
Hexaflumuron	86479-06-3	Keine	18	5	2	9	3	54
Flufenoxuron	101463-69-8	Keine	8	5	4	11	1	44
Creosote	8001-58-9	Keine	8	4	5	8	1	40
Flocoumafen	90035-08-8	2003	14	5	3	10	1	30
Difethialone	104653-34-1	2004	14	5	3	10	1	30
Brodifacoum	56073-10-0	2010	14	4	3	9	1	27
urea metabolite (Flufenoxuron TP)	-	Keine	8	2	4	6	1	24

Tabelle 21: Priorisierung zum Monitoring in terrestrischer Biota (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe, die als „persistent" bewertet werden und einen BCF(Fisch) › 2000 haben.

Ranking TERRESTRISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Triclosan	3380-34-5	Keine	1,2,7,9	potentially yes, to be evaluated further	7	10	4	280
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	potentially yes, to be evaluated further	7	8	4	224
Chlorfenapyr	122453-73-0	Keine	8, 18	yes	3	9	4	108
Hexaflumuron	86479-06-3	Keine	18	yes	2	9	3	54
Flufenoxuron	101463-69-8	Keine	8	yes	4	11	1	44
Creosote	8001-58-9	Keine	8	yes	5	8	1	40
Flocoumafen	90035-08-8	2003	14	yes	3	10	1	30
Difethialone	104653-34-1	2004	14	yes	3	10	1	30

Ranking TERRESTRISCHE BIOTA Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Bodenrelevanz	SCORE (Produkt) Monitoring terrestrisch
Brodifacoum	56073-10-0	2010	14	potentially yes	3	9	1	27
urea metabolite (Flufenoxuron TP)	-	Keine	8	yes	4	6	1	24

Dem beschriebenen Ansatz zur Bewertung von Stoffen für das Monitoring in terrestrischer Biota liegt folgendes Modell zugrunde: die Biozidwirkstoffe gelangen in den Boden und werden dort von Organismen aufgenommen (Aufnahme in Mikroorganismen, über die Mikroorganismen oder auch direkt Aufnahme z.B. in Regenwürmer und weiter in andere Bodenlebewesen, z.B. Igel; terrestrisches Nahrungsnetz).

Für bestimmte Biozide (Rodentizide) ist außerdem ein anderer Pfad relevant: Aufnahme von Wirkstoff aus einem Köder, der nahe eines Gebäudes/einer Siedlung oder in einem Abwasserkanal exponiert wurde, durch Nagetiere (Übergang Anthroposphäre / terrestrische Ökosysteme). Die Nagetiere sind potentielle Beute von Greifvögeln, die durch Sekundärvergiftungen gefährdet sein können. Hierzu können auch die Listen aus den obigen Tabellen zur Identifizierung relevanter Biozide verwendet werden. Relevant sind dabei die Rodentizide (PA 14) aus dieser Liste (die bereits genannten drei Stoffe, die potentiell relevant für Sekundärvergiftungen sind: Flocoumafen, Difethialon, Brodifacoum).

2.7.3 Atmosphärisches Monitoring

Ein Monitoring der Atmosphäre sollte geprüft werden, wenn die Wirkstoffe in die Luft emittiert werden, einen Dampfdruck > 0,01 Pa (oder eine Henry-Konstante > 0,03 Pa m^3 mol^{-1}) und eine atmosphärische Halbwertszeit > 2 Tage aufweisen. Allerdings konnten nicht alle Stoffe bewertet werden, da nicht immer Daten zu Dampfdruck bzw. Henry-Konstante und zur atmosphärischen Halbwertszeit verfügbar waren (insbesondere für TP fehlen diese Daten fast immer). Bei fehlenden Daten werden die Stoffe nicht bewertet (kein Default-Wert vorgesehen). In einigen Fällen konnten Daten zur atmosphärischen Halbwertszeit mittels QSAR abgeschätzt werden (EPI Suite, EPA 2007; Oxidation mit Hydroxyl-Radikalen; Eingabeparameter: 10^6 OH-Radikale)/cm^3, 24 h Tageslicht; falls in den Doc I-Berichten auch AOP-QSAR genutzt wurden, wurden die Ergebnisse unabhängig von den gewählten - aber nicht immer dokumentierten - Eingabeparametern übernommen).

Relevante Stoffe sind solche mit atmosphärenrelevanter PA, Dampfdruck > 0,01 Pa bzw. Henry-Konstante > 0,03 Pa m^3 mol^{-1}, atmosphärischer Halbwertszeit > 2 Tage (Tabelle 22). Die Ergebnisse auf Basis der derzeitigen Datenlage entsprechen denen der Priorisierung im Vorläuferprojekt (keine weiteren relevanten Stoffe bei den neu berücksichtigten Datensätzen).

Tabelle 22: Priorisierung zum Monitoring in der Atmosphäre (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind Stoffe, die einen Dampfdruck › 0,01 Pa oder eine Henry-Konstante › 0,03 Pa m^3 mol^{-1} sowie eine atmosphärische Halbwertszeit › 2 Tage haben.

Ranking ATMOSPHÄRE Substanz	CAS Nr.	PA	Halbwertszeit [d]	SCORE Emission	SCORE Effekte	SCORE Luftrelevanz	SCORE (Produkt) Monitoring Atmosphäre
Hydrogen cyanide	74-90-8	8, 14, 18	535	6	6	3	108
Methylisothiocyanate (MITC) (Dazomet TP)	556-61-6	6, 8, 12	4,5	6	6	1	36
Transfluthrin	118712-89-3	18	2,4	4	6	1	24
Naled	300-76-5	(18)	2,5	3	5	1	15
Cyanamide	420-04-2	3, 18	3,4	5	2	1	10

2.7.4 Kläranlagen-Monitoring

Ein Monitoring von Kläranlagenabläufen sollte geprüft werden, wenn die Wirkstoffe über den Abwasserpfad in Kläranlagen emittiert werden. Es ist davon auszugehen, dass ein Teil der Stoffe dann auch in Oberflächengewässer gelangt. Die priorisierten Stoffe sind in Tabelle 23 gezeigt.

Ein Monitoring von Klärschlamm sollte nach den Kriterien des Vorläuferprojekts geprüft werden, wenn die Wirkstoffe über den Abwasserpfad in Kläranlagen emittiert werden, einen K_{OC} > 10000 aufweisen und persistent sind (Kriterien wie oben bzw. zum Vergleich Persistenz-Kriterien gemäß REACH Annex XIII). Mit diesen Kriterien fallen Stoffe, die in Monitoring-Untersuchungen in Klärschlamm nachgewiesen wurden (und die potentiell bei der landwirtschaftlichen Klärschlammverwendung in Böden gelangen) heraus, z.B. Triclosan und Methyltriclosan (siehe Vergleich mit unterschiedlichen Persistenz- bzw. K_{OC}-Filterkriterien in Tabelle 24 - Tabelle 26). Hier steht aber im Vordergrund, die relevanten Stoffe für die Änderung der Belastung von Klärschlamm zu erfassen. In der Praxis ist bei Untersuchungen das Spektrum für Analysen von Klärschlamm und Kläranlagenabläufen oft ähnlich (siehe z.B. Wick et al. 2010). Es wird deshalb vorgeschlagen, für die Priorisierung für das Monitoring in Klärschlamm die Kriterien gemäß Tabelle 24 zu nutzen.

Tabelle 23: Priorisierung zum Monitoring in Kläranlagenabläufen (TOP 15; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind.

Ranking ABLÄUFE KLÄRANLAGEN Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Triclosan	3380-34-5	Keine	1,2,7,9	5	7	10	3	210
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	2	7	9	3	189
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	7	8	3	168
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	3	8	7	3	168
Alkyldi-methylbenzyl-ammonium chloride (ADBAC)	68424-85-1	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12, 13	0	8	6	3	144
N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (Lonzabac 12)	2372-82-9	Keine	2, 3, 4, 6, 8, 11, 12, 13	0	7	6	3	126
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	2	8	5	3	120
Didecyldimethyl ammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	5	3	120

Ranking ABLÄUFE KLÄRANLAGEN Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	1	7	5	3	105
Didecylmethylpoly(oxy-ethyl) ammonium pro-pionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	5	3	90
DCPP (5-Chloro-2-(4-chlorophenoxy)phenol)	3380-30-1	Keine	1, 2, 4	3	5	6	3	90
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	Keine	7, 8, 9, 10, 11, 21	1	7	4	3	84
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	3	7	4	3	84
NNOOA (DCOIT-TP EW) N-(n-octyl) oxamic acid	-	Keine	7, 8, 9, 10, 11, 21	2	7	4	3	84
Decanoic acid	334-48-5	Keine	4, 18, 19	1	7	4	3	84

Tabelle 24: Priorisierung zum Monitoring in Klärschlamm (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind sowie einen K_{OC} › 10000 haben und die nicht „readily biodegradable“ sind (Punktzahl Persistenz › 0).

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Didecyldimethyl ammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	5	3	120
Didecylmethylpoly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	5	3	90
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	1	54
(AEM 5772 TP) 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	2	3	5	2	30
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	1	27
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	3	8	1	24

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Transfluthrin	118712-89-3	Keine	18	3	4	6	1	24
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	5	3	7	1	21
Cyfluthrin	68359-37-5	2009	18	4	2	10	1	20
Pyriproxyfen	95737-68-1	Keine	18	2	3	6	1	18
Hexaflumuron	86479-06-3	Keine	18	5	2	9	1	18
AEM 5772 (Dimethyloctadecyl[3-(trimethoxysilyl) propyl]ammonium chloride)	27668-52-6	Keine	2, 7, 9	3	3	3	2	18
Triflumuron	64628-44-0	1998	18	2	4	4	1	16
Bis-(N-cyclohexyldiazeniumdioxy)-copper	15627-09-5 / 312600-89-8	Keine	7, 8, 9, 10	2	4	1	2	8
Cyphenothrin	39515-40-7	Keine	18	3	2	3	1	6

Tabelle 25: Priorisierung zum Monitoring in Klärschlamm (alle relevanten Stoffe; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind sowie einen K_{OC} › 10000 haben und im Wasser als „persistent" bewertet werden (bzw. für die keine Bewertung angegeben wurde).

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (im Wasser)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	insufficient data	6	9	1	54
(AEM 5772 TP) 3-(trihydroxysilyl) propy-ldimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	yes (expec-ted)	3	5	2	30
Chlorfenapyr	122453-73-0	Keine	8, 18	yes	3	9	1	27
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	potentially yes (an-aerobic)	3	7	1	21
Hexaflumuron	86479-06-3	Keine	18	no data	2	9	1	18
AEM 5772 (Dime-thyloctadecyl[3-(tri-methoxysilyl) pro-pyl]ammonium chloride)	27668-52-6	Keine	2, 7, 9	yes (expec-ted)	3	3	2	18
Cyphenothrin	39515-40-7	Keine	18	no data	2	3	1	6

Tabelle 26: Priorisierung zum Monitoring in Klärschlamm (TOP 15; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind sowie einen K_{OC} › 100 haben und die nicht „readily biodegradable" sind (Punktzahl Persistenz › 0).

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Triclosan	3380-34-5	Keine	1,2,7,9	5	7	10	3	210
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	2	7	9	3	189
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	7	8	3	168
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	3	8	7	3	168
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	5	3	120
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	2	8	5	3	120
Didecylmethylpoly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	5	3	90

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
DCPP (5-Chloro-2-(4-chlorophenoxy)phenol)	3380-30-1	Keine	1, 2, 4	3	5	6	3	90
Methyl-DCPP (DCPP TP)	-	Keine	1, 2, 4	4	5	5	3	75
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	1	54
Dichlofluanid	1085-98-9	2003	7, 8, 21	3	8	6	1	48
PBC (Propargyl butyl carbamate) (IPBC TP)	76114-73-3	Keine	6, 7, 8, 9, 10, 12, 13	2	8	2	3	48
Tolylfluanid	731-27-1	2010	7, 8, 21	2	6	7	1	42
Thiabendazole	148-79-8	2011	7, 8, 9, 10	3	4	4	2	32
(AEM 5772 TP) 3-(trihydroxysilyl) propy-ldimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	2	3	5	2	30

2.8 Sensitivitätsanalyse

Zunächst wurde eine Sensitivitätsanalyse für das Ranking von Stoffen für das Monitoring in Oberflächengewässern (Wasserphase) durchgeführt. Dabei sollte geprüft werden, ob einer der Bewertungsschritte dominierenden Einfluss auf die Priorisierung hat (d.h., ob sich das Stoffranking ändert, wenn einer der Schritte nicht berücksichtigt wird).

Exemplarisch wird das Ranking der Top 10-Stoffe für das Monitoring in der Wasserphase gezeigt, wenn nur ein Teil der Parameter bewertet wird. Das Ergebnis ist in Tabelle 27 - Tabelle 30 dargestellt. Für die drei Bewertungsschritte sind maximal 6 - 10 Punkte erreichbar. Die hoch gereihten Stoffe erzielen meistens in mindestens zwei Bewertungskategorien hohe Punktzahlen. Wenn eine Bewertungskategorie wegfällt, erscheinen jeweils einige vorher niedriger gereihte Stoffe im Ranking, während andere herausfallen. Die Änderungen sind am größten, wenn die Wirkungsrelevanz nicht berücksichtigt wird (Tabelle 29). In diesem Falle sind beispielsweise DCOIT, Triclosan und Methyltriclosan nicht mehr unter den Top 10 vertreten, während verschiedene Transformationsprodukte neu erscheinen.

Eine weitere Sensitivitätsanalyse wurde für das Ranking von Stoffen für das Monitoring in Klärschlamm durchgeführt. Die Ergebnisse sind in den folgenden Tabellen dargestellt (Tabelle 31 - Tabelle 34). Wiederum sind die Ergebnisse sehr ähnlich bei allen Varianten. Das Ranking verändert sich auch hier am deutlichsten, wenn keine Wirkungsaspekte berücksichtigt werden (dann fallen z.B. d-Phenothrin, Cyfluthrin und Pyriproxyfen heraus, während Bis-(N-cyclohexyldiazeniumdioxy)-Kupfer, AEM 5772 und Triflumuron in die TOP 10 aufsteigen (Tabelle 33).

Tabelle 27: Priorisierung zum Monitoring in der Wasserphase (TOP 10; nur Biozide ohne PSM-Zulassung); Priorisierungskriterien aus dem Vorprojekt plus K_{OC} ‹ 100000; nicht „readily biodegradable“ (Persistenz › 0 Punkte), Multiplikation zur Score-Berechnung; Stand Daten und Zulassungsentscheidungen Februar 2014.

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasser-relevanz	SCORE (Produkt) Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	2	7	9	6	378
Triclosan	3380-34-5	Keine	1,2,7,9	5	7	10	4	280
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	3	8	7	5	280
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	2	8	5	6	240
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	7	8	4	224
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	1	7	5	6	210
Dichlofluanid	1085-98-9	2003	7, 8, 21	3	8	6	4	192
Tolylfluanid	731-27-1	2010	7, 8, 21	2	6	7	4	168
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	Keine	7, 8, 9, 10, 11, 21	1	7	4	6	168
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	3	7	4	6	168

Tabelle 28: Priorisierung zum Monitoring in der Wasserphase (TOP 10; nur Biozide ohne PSM-Zulassung); Priorisierungskriterien aus dem Vorprojekt plus K_{OC} < 100000; nicht „readily biodegradable" (Persistenz > 0 Punkte), Multiplikation zur Score-Berechnung; Stand Daten und Zulassungsentscheidungen Februar 2014 - ohne Bewertung der Emissionsrelevanz (Faktor = 1).

Ranking WASSER	CAS Nr.	PSM Status	PA	Persistenz	SCORE	SCORE	SCORE	SCORE (Produkt)
Substanz		Zulassung bis		(als Score)	Emission	Effekte	Wasser-relevanz	Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	2	1	9	6	54
Triclosan	3380-34-5	Keine	1,2,7,9	5	1	10	4	40
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	3	1	7	5	35
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	1	8	4	32
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	2	1	5	6	30
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	1	1	5	6	30
Tolylfluanid	731-27-1	2010	7, 8, 21	2	1	7	4	28
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	1	9	3	27
Chlorfenapyr	122453-73-0	Keine	8, 18	3	1	9	3	27
Dichlofluanid	1085-98-9	2003	7, 8, 21	3	1	6	4	24

Tabelle 29: Priorisierung zum Monitoring in der Wasserphase (TOP 10; nur Biozide ohne PSM-Zulassung); Priorisierungskriterien aus dem Vorprojekt plus K_{OC} < 100000; nicht „readily biodegradable" (Persistenz > 0 Punkte), Multiplikation zur Score-Berechnung; Stand Daten und Zulassungsentscheidungen Februar 2014 - ohne Bewertung der Wirkungsrelevanz (Faktor = 1).

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasser-relevanz	SCORE (Produkt) Monitoring im Wasser
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	2	8	1	6	48
PBC (Propargyl butyl carbamate) (IPBC TP)	76114-73-3	Keine	6, 7, 8, 9, 10, 12, 13	2	8	1	6	48
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	Keine	7, 8, 9, 10, 11, 21	1	7	1	6	42
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	Keine	7, 8, 9, 10, 11, 21	1	7	1	6	42
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	Keine	7, 8, 9, 10, 11, 21	3	7	1	6	42
NNOOA (DCOIT-TP EW) N-(n-octyl) oxamic acid	-	Keine	7, 8, 9, 10, 11, 21	2	7	1	6	42
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	3	8	1	5	40
Decanoic acid	334-48-5	Keine	4, 18, 19	1	7	1	5	35

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasser-relevanz	SCORE (Produkt) Monitoring im Wasser
C(M)IT (5-chloro-2-methyl-4-isothiazolin-3-one)	26172-55-4	Keine	2, 4, 6, 11, 12, 13	1	7	1	5	35
Nonanoic acid	112-05-0	Keine	2, 10, 19	1	7	1	5	35

Tabelle 30: Priorisierung zum Monitoring in der Wasserphase (TOP 10; nur Biozide ohne PSM-Zulassung); Priorisierungskriterien aus dem Vorprojekt plus K_{OC} ‹ 100000; nicht „readily biodegradable“ (Persistenz › 0 Punkte), Multiplikation zur Score-Berechnung; Stand Daten und Zulassungsentscheidungen Februar 2014 - ohne Bewertung der Relevanz für das Kompartiment (Faktor = 1).

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Wasser-relevanz	SCORE (Produkt) Monitoring im Wasser
Triclosan	3380-34-5	Keine	1,2,7,9	5	7	10	1	70
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	Keine	2, 6, 9, 11, 12, 13	3	8	7	1	56
Methyltriclosan (Triclosan TP)	4640-01-1	Keine	1,2,7,9	5	7	8	1	56
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	1	54
Dichlofluanid	1085-98-9	2003	7, 8, 21	3	8	6	1	48
Tolylfluanid	731-27-1	2010	7, 8, 21	2	6	7	1	42
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	Keine	6, 7, 8, 9, 10, 12, 13	2	8	5	1	40
Creosote	8001-58-9	Keine	8	4	5	8	1	40
Cybutryne (Irgarol)	28159-98-0	Keine	21	4	5	8	1	40
Hydrogen cyanide	74-90-8	2001	8, 14, 18	2	6	6	1	36

Tabelle 31: Priorisierung zum Monitoring in Klärschlamm (TOP 10; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind sowie einen K_{OC} › 10000 haben und die nicht „readily biodegradable" sind (Punktzahl Persistenz › 0).

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	5	3	120
Didecylmethylpoly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	5	3	90
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	1	54
(AEM 5772 TP) 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	2	3	5	2	30
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	1	27
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	3	8	1	24
Transfluthrin	118712-89-3	Keine	18	3	4	6	1	24

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	5	3	7	1	21
Cyfluthrin	68359-37-5	2009	18	4	2	10	1	20
Pyriproxyfen	95737-68-1	Keine	18	2	3	6	1	18

Tabelle 32: Priorisierung zum Monitoring in Klärschlamm (TOP 10; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind sowie einen K_{OC} › 10000 haben und die nicht „readily biodegradable" sind (Punktzahl Persistenz › 0) - ohne Berücksichtigung der Emissionsrelevanz (Faktor = 1).

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	1	5	3	15
Didecylmethylpoly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	1	5	3	15
(AEM 5772 TP) 3-(trihydroxy-silyl) propyldimethylocta-decyl ammonium chloride	199111-50-7	Keine	2, 7, 9	2	1	5	2	10
Cyfluthrin	68359-37-5	2009	18	4	1	10	1	10
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	1	9	1	9
Chlorfenapyr	122453-73-0	Keine	8, 18	3	1	9	1	9
Hexaflumuron	86479-06-3	Keine	18	5	1	9	1	9

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Chrysanthemum cinerariae-folium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	1	8	1	8
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	5	1	7	1	7
Transfluthrin	118712-89-3	Keine	18	3	1	6	1	6

Tabelle 33: Priorisierung zum Monitoring in Klärschlamm (TOP 10; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind sowie einen K_{OC} › 10000 haben und die nicht „readily biodegradable" sind (Punktzahl Persistenz › 0) -ohne Berücksichtigung der Wirkungsrelevanz (Faktor = 1).

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	1	3	24
Didecylmethylpoly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	1	3	18
Bis-(N-cyclohexyl-diazenium-dioxy)-copper	15627-09-5 / 312600-89-8	Keine	7, 8, 9, 10	2	4	1	2	8
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	1	1	6
(AEM 5772 TP) 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride	199111-50-7	Keine	2, 7, 9	2	3	1	2	6
AEM 5772 (Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride)	27668-52-6	Keine	2, 7, 9	3	3	1	2	6

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Transfluthrin	118712-89-3	Keine	18	3	4	1	1	4
Triflumuron	64628-44-0	1998	18	2	4	1	1	4
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	1	1	3
Chrysanthemum cinera-riaefolium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	3	1	1	3

Tabelle 34: Priorisierung zum Monitoring in Klärschlamm (TOP 10; nur Biozide ohne PSM-Zulassung); Stand Daten und Zulassungsentscheidungen Februar 2014. Berücksichtigt sind alle Stoffe, die abwasserrelevant sind sowie einen K_{OC} › 10000 haben und die nicht „readily biodegradable“ sind (Punktzahl Persistenz › 0) - ohne Berücksichtigung der Kläranlagenrelevanz (Faktor = 1).

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagen-relevanz	SCORE (Produkt) Monitoring Kläranlagen
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	6	9	1	54
Didecyldimethylammonium chloride (DDAC)	7173-51-5	Keine	1, 2, 3, 4, 6, 8, 10, 11, 12	1	8	5	1	40
Didecylmethylpoly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	Keine	2, 4, 8, 9, 10, 11, 12	4	6	5	1	30
Chlorfenapyr	122453-73-0	Keine	8, 18	3	3	9	1	27
Chrysanthemum cinerariae-folium, Extract	8003-34-7 / 89997-63-7	Keine	18	2	3	8	1	24
Transfluthrin	118712-89-3	Keine	18	3	4	6	1	24
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	5	3	7	1	21
Cyfluthrin	68359-37-5	2009	18	4	2	10	1	20

Ranking KLÄRSCHLAMM Substanz	CAS Nr.	PSM Status Zulassung bis	PA	Persistenz (als Score)	SCORE Emission	SCORE Effekte	SCORE Kläranlagenrelevanz	SCORE (Produkt) Monitoring Kläranlagen
Pyriproxyfen	95737-68-1	Keine	18	2	3	6	1	18
Hexaflumuron	86479-06-3	Keine	18	5	2	9	1	18

Mit dem vorhandenen Datensatz wurde auch versucht, eine Auswertung für das Oberflächengewässer-Monitoring in Anlehnung an das Schweizer Vorgehen (I. Wittmer, Beitrag auf dem Biocides Monitoring Workshop, Berlin, November 2012; siehe Jäger et al. 2013) durchzuführen (für den Bewertungspfad für Stoffe, für die keine Monitoringdaten vorliegen). Dazu wurden folgende Parameter verwendet: log $K_{OW} < 5$, PNEC < 0.1 µg/L, DT50 Wasser > 1 d. Das Ergebnis ist in Tabelle 35 zusammengestellt. Mit diesem Vorgehen wurden für die Schweiz priorisiert: DEET, Mecoprop, Diuron, Carbendazim, Diazinon, Triclosan, Thiamethoxam, Tebuconazol, Terbutryn, Irgarol/Cybutryn (Workshop-Beitrag I. Wittmer). Von diesen priorisierten Stoffen sind nur Triclosan und Cybutryn in der Liste in Tabelle 35 enthalten (für einige der Stoffe der Schweizer Liste, z.B. Carbendazim oder Terbutryn, lagen allerdings keine EU Assessment Reports vor, so dass sie hier nicht berücksichtigt werden konnten). Tebuconazol fällt z.B. aufgrund einer unterschiedlichen Datenbasis heraus, da im hier berücksichtigten Assessment Report eine PNEC > 0.1 µg/L angegeben ist (Berücksichtigung beim Schweizer Vorgehen evtl. auf Basis von vorliegenden Monitoringdaten mit Konzentrationswerten oberhalb der PNEC/UQN).

Tabelle 35: Priorisierung zum Monitoring in der Wasserphase (alle relevanten Stoffe inklusive Biozide mit PSM-Zulassung); Priorisierungskriterien gemäß dem Vorschlag aus der Schweiz (I. Wittmer, Beitrag auf dem Biocides Monitoring Workshop, Berlin, Februar 2014): log K_{OW} ‹ 5, PNEC ‹ 0,1 µg/L, DT50 Wasser › 1 d.

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	Keine	7, 8, 9, 10, 11, 21	7	9	6	378
Triclosan	3380-34-5	Keine	1,2,7,9	7	10	4	280
Diflubenzuron	35367-38-5	›2013	18	4	9	2	72
Spinosad	168316-95-8	›2013	3, 18	4	6	3	72
Clothianidin	210880-92-5	›2013	8, 18	4	6	3	72
Clothianidin (CGA 322704) (Thiametho-xam TP)	210880-92-5	›2013	8, 18	4	5	3	60
Copper pyrithione	14915-37-8	Keine	21	5	11	1	55
Prallethrin	103065-19-6	Keine	18	3	7	2	42
Fenpropimorph	67564-91-4	›2013	8	5	8	1	40
Bendiocarb	22781-23-3	2003	18	4	5	2	40
Cybutryne (Irgarol)	28159-98-0	Keine	21	5	8	1	40
Fenoxycarb	72490-01-8	2013	8	4	9	1	36
Fipronil	120068-37-3	Keine	18	3	6	2	36

Ranking WASSER Substanz	CAS Nr.	PSM Status Zulassung bis	PA	SCORE Emission	SCORE Effekte	SCORE Wasserrelevanz	SCORE (Produkt) Monitoring im Wasser
Triflumuron	64628-44-0	1998	18	4	4	2	32
Abamectin	71751-41-2	›2013	18	2	7	2	28

Außerdem wurde das Ranking für die Emissionsrelevanz mit den Verbrauchsmengen der Wirkstoffe verglichen. Da für Deutschland derzeit keine Mengenangaben vorliegen, wurden Daten aus Belgien verwendet (Marktstudie mit Daten für das Jahr 2011 ist verfügbar; SPF 2012). Es wird angenommen, dass die Anwendungsmuster in Deutschland und Belgien ähnlich sind (der Gesamtverbrauch ist hier zunächst weniger relevant).

Die hier errechnete Punktzahl für die Emissionsrelevanz basiert auf der Produktionsmengen-Bewertung (HPVC/LPVC nach ESIS) und der Anzahl der gemeldeten Produkte (BAuA-Melderegister). Als Maß für eine disperse Nutzung wird auch die Verwendung in mehreren PA berücksichtigt. Insofern wäre in diesem Konzept zu prüfen, welche Auswirkungen der Ersatz der ESIS-Angaben durch die Mengenangabe hat.

Die Gegenüberstellung in Tabelle 36 (Biozide mit höchster Emissionsrelevanz im Datenbestand) zeigt, dass die in Belgien erfassten Verbrauchsmengen für einige Stoffe deutlich unter der Abschätzung liegen (Dichlofluanid: kein Verbrauch in 2011; IPBC und DCOIT nur geringe Verbrauchsmengen).

Tabelle 36: Vergleich der Ergebnisse der Bewertung der Emissionsrelevanz mit dem Verbrauch in Belgien (SPF 2012).

Stoff	CAS No.	Relevante PA	Anzahl Produkte BAuA-Register	ESIS (HPVC/ LPVC/-)	Gesamt-punkte Emission#	Verbrauch in Belgien t (in 2011)
Propan-2-ol	67-63-0	1, 2, 4	ca. 1500	HPVC	9	157
Sodium hypochlorite	7681-52-9	1, 2, 3, 4, 5, 11, 12	› 1500	HPVC	9	1749
Propan-1-ol	71-23-8	1, 2, 4	ca. 500	HPVC	8	47
Dichlofluanid	1085-98-9	7, 8, 21	190	HPVC	8	0
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	6, 7, 8, 9, 10, 12, 13	1500	LPVC	8	13
Alkyldimethylbenzyl-ammonium Chloride (ADBAC)	68424-85-1	1, 2, 3, 4, 6, 8, 10, 11, 12, 13	› 1500	LPVC	8	137
Lactic acid	79-33-4	2, 3, 4, 6	240	HPVC	8	7
Glutaraldehyde	111-30-8	1, 2, 3, 4, 6, 11, 12, 13	900	HPVC	8	217
Calcium hypochlorite	7778-54-3	2, 3, 4, 5, 11	320	HPVC	8	30
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	2, 6, 9, 11, 12, 13	941	HPVC	8	58

Stoff	CAS No.	Relevante PA	Anzahl Produkte BAuA-Register	ESIS (HPVC/ LPVC/-)	Gesamt-punkte Emission#	Verbrauch in Belgien t (in 2011)
Didecyldimethylam-monium chloride (DDAC)	7173-51-5	1, 2, 3, 4, 6, 8, 10, 11, 12	›1500	LPVC	8	220
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	7, 8, 9, 10, 11, 21	230	LPVC	7	11

Kriterien für die Punkteberechnung siehe Kapitel 2.3.

In einer Untersuchung in der Schweiz wurde eine Mengenabschätzung von Bioziden in Schutzmitteln (Bautenfarben und -putze PA 7, Holz PA 8, Mauerwerk PA 10 und Antifouling PA 21) vorgenommen (Burkhardt und Dietschweiler 2013). Die Mengenangaben umfassen allerdings weite Bereiche (z.B. bei PA 8: 4,8 - 48 Tonnen pro Jahr; keine Zuordnung zu einzelnen Wirkstoffen; wichtigste Wirkstoffe in dieser PA in der Schweiz: IPBC, Propiconazol, Tebuconazol) und lassen sich für die Fragestellung der Priorisierung nur schwer verwenden (auch, weil die meisten Wirkstoffe nicht nur in den untersuchten vier, sondern auch in anderen PA verwendet werden). Allerdings sind die Informationen, welche Stoffe in welcher PA am häufigsten bzw. gar nicht mehr verwendet werden, hilfreich für Plausibilitätsprüfungen. Für hier bewertete und teilweise hoch gereihte Stoffe werden in der Schweiz folgende (nur niedrige) Jahresmengen eingesetzt: < 1 t IPBC bzw. DCOIT für PA 7; < 1 t QAV (Wirkstoffe nicht spezifiziert) für PA 10; 1 - 2 t Dichlofluanid bzw. Tolylfluanid für PA 21. Nach dieser Untersuchung wird in der Schweiz der Wirkstoff Cybutryn (Irgarol) nicht mehr in PA 21 eingesetzt.

3 Diskussion des Priorisierungskonzepts für das Monitoring von Bioziden

Zur Übersicht sind die hier in diesem Bericht verwendeten Kriterien für die Priorisierung von Bioziden für ein Umweltmonitoring in Tabelle 37 zusammengestellt. Die Aggregation der Ergebnisse der drei Bewertungsschritte erfolgt durch Multiplikation. Das resultierende Produkt wird dann zur Priorisierung von Biozide für das Monitoring in den verschiedenen Kompartimenten genutzt (teilweise unter Berücksichtigung weiterer Kriterien wie Persistenz oder Bodenmobilität).

Tabelle 37: Im Priorisierungskonzepts für das Monitoring von Bioziden verwendete Kriterien.

Schritt 1: Abschätzung der Emissionsrelevanz von Biozidwirkstoffen
Emissionsrelevante Produktart: PA 1, 2, 3, 4, 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 (siehe Kapitel 1); je PA 1 Punkt (maximal 3 Punkte)
Anzahl Produkte mit dem Wirkstoff im BAuA-Melderegister: bis zu 10 Produkte: 0 Punkte; 11 - 100 Produkte: 1 Punkt; 101 - 1000 Produkte: 2 Punkte; › 1000 Produkte: 3 Punkte
Produktions- bzw. Importmengen (ESIS-Datenbank, http://esis.jrc.ec.europa.eu): ‹ 10 t/a: 0 Punkte; 10 - 1000 t/a (low production volume chemical, LPVC): 2 Punkte; › 1000 t/a (high production volume chemical, HPVC): 3 Punkte; Default-Wert (Stoff nicht gelistet oder unklare Angabe zur Produktions-/Importmenge): 1 Punkt.
Schritt 2: Bewertung der Relevanz der ökotoxikologischen Wirkung von Biozidwirkstoffen
PNEC Wasser; PNECs für aquatische Organismen werden wie folgt klassifiziert: PNEC ‹ 0,01 ug/L: 4 Punkte; 0,01 - 0,1 ug/L: 3 Punkte; › 0,1 - 1 ug/L: 2 Punkte; › 1 - 10 ug/L: 1 Punkt; › 10 ug/L: 0 Punkte. Wenn keine Daten angegeben sind (z.B. bei Transformationsprodukten) wird ein Default-Wert verwendet (1 Punkt)
PEC/PNEC-Vergleich im Dossier: PEC/PNEC › 1 für mehr als ein Szenario: 2 Punkte; PEC/PNEC › 1 für ein Szenario: 1 Punkt; PEC/PNEC für alle Szenarien ‹ 1: 0 Punkte; keine Daten: Default-Wert = 1 Punkt
T-Klassifizierung nach CLP: T+: 3 Punkte; T: 2 Punkte; weder T+ noch T: 0 Punkte; Default-Wert: 1 Punkt
Bioakkumulation im Fisch: Biokonzentrationsfaktor (BCF) ‹ 100: 0 Punkte; BCF › 100 - 2000: 1 Punkt; BCF › 2000: 2 Punkte; BCF › 5000: 3 Punkte
Schritt 3: Bewertung der Relevanz von Umweltkompartimenten für ein Umweltmonitoring von Biozidwirkstoffen (auf Basis der Nutzung für verschiedene PA und des Verteilungs-/Abbauverhaltens der Wirkstoffe)
Berücksichtigung der Emissionsrelevanz der einzelnen Produktarten (PA) für das jeweilige Kompartiment Oberflächengewässer: PA 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 (zusätzlich indirekte Einträge über Kläranlagen, s.u.);

Böden: PA 7, 8, 10, 14, 18, 19 (zusätzlich indirekte Einträge über Kläranlagen/Klärschlamm, s.u., und Gülle: PA 3, 18); Atmosphäre: PA 8, 11, 14, 18; Kläranlagen: PA 1, 2, 3, 4, 7, 10, 11, 12, 18 19; Je notifizierter PA wird 1 Punkt zugeordnet (maximal 3 Punkte)
Angaben zur leichten biologischen Abbaubarkeit und zur Persistenz: leicht biologisch abbaubar: 0 Punkte; nicht leicht biologisch abbaubar: 2 Punkte; keine Angaben bzw. nicht anwendbar (z.B. bei anorganischen Metallverbindungen): 1 Punkt; P-Kriterium gemäß REACh Annex XIII erfüllt: 2 Punkte; vP-Kriterium erfüllt: 3 Punkte; P-Kriterium nicht erfüllt: 0 Punkte; keine Angaben bzw. nicht anwendbar (z.B. bei anorganischen Metallverbindungen): 1 Punkt; für die Abbildung dieses Kriteriums wird die Summe gebildet aus den beiden Bewertungen für die leichte biologische Abbaubarkeit und die Persistenz
Kompartimentspezifische Parameter
Wasser: Stoffe mit wasserrelevanter PA, nicht leicht biologisch abbaubar, Verteilungskoeffizient organischer Kohlenstoff-Wasser $K_{OC} < 100000$
Aquatische Biota: Stoffe mit wasserrelevanter PA, nicht leicht biologisch abbaubar, Biokonzentrationsfaktor BCF(Fisch) > 100
Sediment/Schwebstoffe: Stoffe mit wasserrelevanter PA, nicht leicht biologisch abbaubar, Verteilungskoeffizient organischer Kohlenstoff-Wasser $K_{OC} > 10000$
Boden: Stoffe mit bodenrelevanter PA, nicht leicht biologisch abbaubar, Verteilungskoeffizient organischer Kohlenstoff-Wasser $K_{OC} > 10000$
Grundwasser: Stoffe mit bodenrelevanter PA, „Groundwater Ubiquity Score“ GUS $> 2{,}8$ (berechnet, wenn Angaben zu K_{OC} und DT50 verfügbar sind)
Terrestrische Biota: Stoffe mit bodenrelevanter PA, nicht leicht biologisch abbaubar, Biokonzentrationsfaktor BCF(Fisch) > 2000
Atmosphäre: Stoffe mit luftrelevanter PA, Dampfdruck $> 0{,}01$ Pa (oder eine Henry-Konstante $> 0{,}03$ Pa m^3 mol^{-1}) und atmosphärische Halbwertszeit $>$ 2 Tage
Kläranlagenabläufen: alle Stoffe mit kläranlagenrelevanter PA
Klärschlamm: alle Stoffe mit kläranlagenrelevanter PA, nicht leicht biologisch abbaubar, Verteilungskoeffizient organischer Kohlenstoff-Wasser $K_{OC} > 10000$

aufgrund der Datenlage Verwendung des Fisch-BCF.

Zur Plausibilitätsprüfung wird ein Vergleich der Stoffe, die hier als prioritär identifiziert wurden, mit den Ergebnissen der Umfrage im Vorläuferprojekt (Rüdel und Knopf 2012; Abgleich mit den Fragebogenlisten und - soweit verfügbar - auch mit Messdaten) und der Literaturrecherche (separates Arbeitspaket im laufenden Vorhaben) durchgeführt. Allerdings ist zu beachten, dass nur ca. 135 vorwiegend „nicht leicht biologisch abbaubare“ Biozidwirkstoffe im Testdatensatz enthalten sind. Für die anderen Biozidwirkstoffe, die derzeit noch im Rahmen des Review-Programms bewertet werden, kann zunächst keine Plausibilitätsprüfung durchgeführt werden. Darunter sind auch Stoffe, die häufig im Monitoring nachgewiesen werden (z.B. Isoproturon, Terbutryn oder Diuron, die allerdings auch PSM-Wirkstoffe sind bzw. bis vor kurzem waren).

Für ein Monitoring in den entsprechenden Matrices wurden folgende Stoffe identifiziert (ohne bislang nicht im Monitoring untersuchte Biozid-TP; unterstrichen: in Untersuchungsprogrammen der Bundesländer oder in der Untersuchung von Wick et al., 2010, enthalten; fett: Nachweis in Matrix oberhalb der Bestimmungsgrenze).

Oberflächengewässer (Tabelle 7):

DCOIT, **Triclosan**, **BIT**, IPBC, **Methyltriclosan (Triclosan TP)**, Dichlofluanid, Tolylfluanid, Permethrin, Blausäure, Decansäure, MITC, C(M)IT, **DMSA (Dichlofluanid TP)**, Margosa-Extrakt, MIT.

Aquatische Biota (Tabelle 9):

DCOIT, **Triclosan**, **Methyltriclosan (Triclosan TP)**, Permethrin, Flufenoxuron, Chlorfenapyr, Chrysanthemum-Extrakt, Transfluthrin, Flufenoxuron, d-Phenothrin, Prallethrin, Kreosot, Cyfluthrin, Irgarol/Cybutryn, Fenoxycarb.

Schwebstoffe/Sedimente (Tabelle 12):

DDAC, Bardap 26, **Permethrin**, Chlorfenapyr, Chrysanthemum-Extrakt, Transfluthrin, Flufenoxuron, d-Phenothrin, Kreosot, Cyfluthrin, Pyriproxyfen, Hexaflumuron, Triflumuron, Flocoumafen.

Grundwasser (Tabelle 16):

DMSA (Dichlofluanid TP), MITC (Dazomet TP), C(M)IT, Fipronil, MIT, Warfarin.

Kläranlagenabläufe (Tabelle 23):

Triclosan, DCOIT, **Methyltriclosan (Triclosan TP)**, BIT, ADBAC, Lonzabac 12, IPBC, DDAC, Bardap 26, DCPP, Decansäure.

Klärschlamm (Tabelle 24):

DDAC, Bardap 26, Permethrin, Chlorfenapyr, Chrysanthemum-Extrakt, Transfluthrin, d Phenothrin, Cyfluthrin, Pyriproxyfen, Hexaflumuron, AEM 5772, Triflumuron, Bis-(N-cyclohexyldiazenium-dioxy)-Kupfer (Cu-HDO), Cyphenothrin.

Bei den Stofflisten für Klärschlamm und Kläranlagenabläufe ist zu berücksichtigen, dass hier eine Differenzierung aufgrund des Verteilungsverhaltens (K_{OC}) durchgeführt wird. Ein Monitoring sollte entweder im Schlamm oder im Ablauf erfolgen. In Untersuchungen werden dagegen häufig gleiche Parameter im Schlamm und im Ablauf gemessen (siehe z.B. Wick et al. 2010). In der Kläranlage verteilt sich Triclosan beispielsweise zu ähnlichen Anteilen in Schlamm und in der Wasserphase. Für ein Trendmonitoring könnten damit prinzipiell beide Kompartimente genutzt werden.

Eine Plausibilitätsprüfung für das Kompartiment Boden war im Rahmen dieses Projekts nicht möglich, da bei der Literaturrecherche bislang kaum Monitoring-Daten gefunden wurden. Einzelne Untersuchungen wurden beispielsweise auf Fipronil und Rodentizide durchgeführt. Auch in der im Vorläuferprojekt durchgeführten Umfrage wurde zwar von Untersuchungen von Böden berichtet, aber keine zum Vergleich nutzbaren Monitoring-Ergebnisse zur Verfügung gestellt (es waren auch keine der hier für Boden priorisierten Biozide untersucht worden).

Für die für ein mögliches Luft-Monitoring priorisierten Stoffe konnte kein Abgleich mit Monitoring-Daten erfolgen, da anscheinend bislang keine derartigen Untersuchungen durchgeführt werden.

4 Ausblick

Für die Umsetzung eines Biozidmonitoring-Programms können die folgenden Empfehlungen abgeleitet werden:

Oberflächengewässer (limnische Gewässer, Wasserphase und Sedimente/Schwebstoffe): da Monitoring-Daten zu Bioziden bei den Überwachungsuntersuchungen gemäß WRRL bzw. OGewV anfallen, kann hier in einem ersten Schritt leicht ein Überblick erhalten werden (räumliche und zeitliche Vergleiche). Die Daten von LAWA-Übersichtsmessstellen aller Bundesländer sind im UBA vorhanden. Daten von operativen Messstellen wären gegebenenfalls zur Ergänzung bei den Bundesländern abzufragen. Parallel zur Untersuchung von Biozidwirkstoffen im Oberflächengewässer-Monitoring (Wasserphase) sollten geeignete Tracer mit untersucht werden, die für Belastungen durch Abwassereinleitungen typisch sind (z.B. Methyltriclosan, Balmer et al. 2004; Arzneimittelwirkstoffe wie Diclofenac, Wittmer et al. 2011; Süßstoff Acesulfam, Buerge und Poiger 2011). Hieraus lassen sich dann für Wirkstoffe, die sowohl als Biozid- als auch als Pflanzenschutzmittel-Wirkstoff eingesetzt werden, evtl. Rückschlüsse auf die Ursache einer Belastung ableiten (z.B. Kläranlagenablauf versus Pflanzenschutz-Anwendung).

Oberflächengewässer (marine Gewässer, Wasserphase und Sedimente): PA 21-Wirkstoffe in Marinas und küstennahe Gebiete (die Belastungen im Bereich der küstenfernen Nord- und Ostsee sind vermutlich gering).

Aquatische Biota: für bioakkumulierende Biozidwirkstoffe, die in Gewässer eingetragen werden, kann ein Monitoring von Fischen oder anderen aquatischen Organismen sinnvoll sein. Hier bietet es sich an, die Umweltprobenbank des Bundes (UPB) zu nutzen. Im Archiv der UPB sind Proben von Fischen und Dreikantmuscheln verfügbar, die über Jahre gesammelt wurden und die Untersuchungen einer Vielzahl von insbesondere lipophilen Stoffen erlauben (Rüdel und Schröter-Kermani 2006). Untersuchungen zu Methyltriclosan belegen die Anwendbarkeit (Rüdel et al. 2013).

Klärschlamm: bisherige Untersuchungen belegen die Relevanz des Eintrags von Biozidwirkstoffen aus Haushalten über den Abwasserpfad. Stoffe können über verschiedene Mechanismen an Klärschlamm adsorbieren (soweit die Stoffe nicht leicht bioabbaubar sind). Die Überschneidung mit Anwendungen entsprechender Wirkstoffe in Pflanzenschutzmitteln ist insbesondere in städtischen Regionen vermutlich gering (aber evtl. Einträge durch z.B. Herbizid-Anwendungen im Haus und Garten).

Kläranlagenabläufe: bisherige Untersuchungen belegen die Relevanz des Eintrags von Biozidwirkstoffen über Kläranlagenabläufe in Gewässer (auch bei leicht bioabbaubaren Stoffen, die in hohen Mengen in Kläranlagen eingebracht werden).

Böden: derzeit nur wenige, vorwiegend negative Befunde. Bislang werden keine regelmäßigen Monitoring-Untersuchungen durchgeführt. Es wird vorgeschlagen, ein Screening auf Flächen, auf denen Gülle bzw. Klärschlamm ausgebracht wird, durchzuführen (vermutlich relevantester Eintrag abgesehen von lokalen Einträgen durch Biozidanwendungen).

Wildtier-Monitoring: es wird vorgeschlagen, ein Monitoring auf Rodentizide in Nagetieren bzw. in Räubern von Nagetieren (Greifvögel) durchzuführen. Hierbei sollten die Erfahrungen aus dem laufenden UBA Forschungsvorhaben „Erfassung von Rückständen von als Rodentizid ausgebrachten Antikoagulantien in wildlebenden Biota“ (FKZ 3710 63 401) berücksichtigt werden. Ergebnisse aus anderen Staaten geben Hinweise auf eine Belastung von Organismen in terrestrischen Ökosystemen (Christensen et al. 2012; Hughes et al. 2013; Walker et al. 2012; siehe auch Workshop-Bericht, Jäger et al. 2013). Einige der als Rodentizide eingesetzten Wirkstoffe sind als PBT-Stoffe klassifiziert. Es wird eine Kooperation mit dem Leibniz-Institut für Zoo- und Wildtierforschung (IZW) in Berlin empfohlen, da dort bereits eine Probenbank von Greifvögel-Proben (z.B. Leber und andere Organe) existiert, so dass retrospektive Untersuchungen möglich sind.

Für ein spezifisches Monitoring von Biozidwirkstoffen sollten die mit dem hier vorgeschlagenen Vorgehen als relevant für die entsprechenden Umweltkompartimente identifizierten Biozidwirkstoffe untersucht werden (möglichst nach Priorisierung auf Basis einer größeren Stoffanzahl, d.h. aller weiteren relevanten Wirkstoffe aus dem Review-Programm). Die Untersuchungen sollten sich auf die gemäß der Priorisierung relevantesten Stoffe konzentrieren. Falls umsetzbar, sollte aber bei der Analytik versucht werden, möglichst viele Stoffe zu erfassen, sofern diese parallel quantifiziert werden können (Multimethode). Dies würde die Datenlage zum Vorkommen von Biozidwirkstoffen in der Umwelt insgesamt verbessern und auch die Möglichkeit einer Absicherung des Priorisierungskonzepts bieten.

5 Quellenverzeichnis

Balmer, M. E., Poiger, T., Droz, C., Romanin, K., Bergqvist, P.,-A. Müller, M. D., Buser, H.-R. (2004): Occurrence of Methyl Triclosan, a Transformation Product of the Bactericide Triclosan, in Fish from Various Lakes in Switzerland. Environ. Sci. Technol. 38, 390-395.

Buerge, I. J., Poiger, T. (2011): Acesulfam: ein künstlicher Süßstoff als Abwasserindikator. Nachr. Chem. 59, 1084-1086.

Burkhardt, M., Dietschweiler, C. (2013): Mengenabschätzung von Bioziden in Schutzmitteln in der Schweiz. Bautenfarben und –putze (PA 7), Holz (PA 8), Mauerwerk (PA 10) und Antifouling (PA 21). HSR Hochschule für Technik Rapperswil / Institut für Umwelt- und Verfahrenstechnik (UMTEC), 8640 Rapperswil, Schweiz. Im Auftrag des Bundesamtes für Umwelt (BAFU), Bern, Schweiz, 24. April 2013.

Christensen, T.K., Lassen, P., Elmeros, M. (2012): High exposure rates of anticoagulant rodenticides in predatory bird species in intensively managed landscapes in Denmark. Arch. Environ. Contam. Toxicol. 63, 437-444.

COWI (2009): Assessment of different options to address risks from the use phase of biocides. Final report on behalf of the European Commission Environment Directorate-General, March 2009. COWI A/S, Kongens Lyngby, Denmark.
http://ec.europa.eu/environment/biocides/pdf/report_use.pdf
http://ec.europa.eu/environment/biocides/pdf/report_use_annex1.pdf
http://ec.europa.eu/environment/biocides/pdf/report_use_annex2.pdf

EPA (2007): EPI Suite, version 4.00. U.S. Environmental Protection Agency EPA.
www.epa.gov/oppt/exposure/pubs/episuite.htm

Gómez-Canela, C., Barata, C., Lacorte, S. (2014): Occurrence, elimination, and risk of anticoagulant rodenticides and drugs during wastewater treatment. Environ. Sci. Pollut. Res. 21, 7194-7203.

Gustafson, D.I. (1989): Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environ. Toxicol. Chem. 8, 339-357.

Hughes, J., Sharp, E., Taylor, M.J., Melton, L., Hartley, G. (2013): Monitoring agricultural rodenticide use and secondary exposure of raptors in Scotland. Ecotoxicology 22, 974-984.

Jäger, S., Dulio, V., Schwarzbauer, J. Slobodnik, J., Rüdel, H. (2013): Environmental monitoring of biocides in Europe – from prioritisation to measurements. Workshop organized by NORMAN, Paris, and Umweltbundesamt, Dessau-Rosslau, November 5–6, 2012 in Berlin. Workshop Report, January 2013.

Kahle, M., Nöh, I. (2009): Biozide in Gewässern - Eintragspfade und Informationen zur Belastungssituation und deren Auswirkungen. UBA-Texte 09/09, Umweltbundesamt, Dessau-Roßlau.
https://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/3811.pdf

McCall, P.J., Laskowski, D. A., Swann, R. L., Dishburger, H. J. (1981): Measurement of Sorption Coefficients of organic Chemicals and their use in Environmental Fate Analysis; Test Protocols for Environmental Fate & Movement of Toxicants. Proceedings of a AOAC-Symposium (21.-22.10.1980). AOAC, Washington, DC.

Rüdel, H., Böhmer, W., Müller, M., Fliedner, A., Ricking, M., Teubner, D., Schröter-Kermani, C. (2013): Retrospective study of triclosan and methyl-triclosan residues in fish and suspended particulate matter: results from the German Environmental Specimen Bank. Chemosphere 91, 1517-1524.

Rüdel, H., A. Fliedner, M. Herrchen (2007): Strategie für ein stoffangepasstes Gewässer-monitoring - Machbarkeitsstudie. Erfassung potenziell sorbierender oder akkumulierender Stoffe in den Kompartimenten Biota, Sedimenten und Schwebstoffen (Projekt für das österreichische Lebensministerium, Wien.

Rüdel, H., Knopf, B. (2012): Vorbereitung eines Monitoring-Konzepts für Biozide in der Umwelt, Abschlussberichtes zu FKZ 360 04 036 des Fraunhofer IME, Schmallenberg für das Umweltbundesamt, Dessau-Roßlau.

Rüdel, H., Schröter-Kermani, C. (2006): Die Umweltprobenbank des Bundes als Instrument zur Untersuchung der Relevanz „Neuer Schadstoffe“ in Gewässern. Mitt. Umweltchem. Ökotox. 12, 8-11.

SPF (2012): Le marché des biocides en Belgique. Suivant les données en possession du SPF 2011, Service Public Fédéral (SPF), Santé Publique, Sécurité de la Chaine alimentaire, Environnement, Direction Générale Environnement, Brussels, March 2012.

Walker, L.A., Llewellyn, N.R., Pereira, M.G., Potter, E.D., Sainsbury, A.W., Shore, R.F. (2012): Anticoagulant rodenticides in predatory birds 2010: a Predatory Bird Monitoring Scheme (PBMS) report. Centre for Ecology & Hydrology, Lancaster, UK.

Wick, A., Fink, G., Ternes, T. A. (2010): Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1217, 2088-2103.

Wittmer, I. K., Scheidegger, R., Bader, H. P., Singer, H., Stamm C. (2011): Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409, 920-932.

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Design of a Biocides Monitoring Programme (Annex 3)

Teilbericht zum Projekt: Umweltbelastung durch Biozide: Erarbeitung der Eckpfeiler eines Monitoring-Messprogrammes für Einträge von Bioziden in die Umwelt

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Kurzbeschreibung

Die EU Biozidprodukte-Verordnung (Nr. 528/2012) verursacht Veränderungen des Einsatzes von Bioziden und folglich ihrer Umweltkonzentrationen. Für Biozide, die in der Liste der zugelassenen Stoffe aufgenommen wurden, könnten die Belastungen ansteigen, während für Stoffe, für die Nichtzulassungsentscheidungen getroffen oder Maßnahmen zur Risikobegrenzung implementiert wurden, verringerte Umweltbelastungen zu erwarten sind. Solche Konsequenzen können durch ein Umweltmonitoring nachgewiesen werden. Dabei könnte auch überprüft werden, ob die Umweltkonzentrationen oberhalb der abgeleiteten Wirkschwellen (z.B. PNECs) liegen. Doch bislang werden Biozide in den meisten Monitoringprogrammen nicht angemessen abgedeckt. Traditionell, z.B. in Gewässern, werden vor allem Pflanzenschutzmittel (teilweise auch als Biozide zugelassen), Stoffe, die aus industriellen Quellen stammen, und bestimmte ubiquitäre Schadstoffe überwacht. Ziel dieses Projekts ist, einen Vorschlag für ein umfassendes Monitoringkonzept für Biozide zu erarbeiten. Hauptzweck ist, eine bessere Berücksichtigung von Bioziden in bestehenden Monitoringprogrammen zu erreichen. Als erster Schritt wurden relevante Kompartimente identifiziert und relevante Biozide priorisiert. Diese Listen werden Monitoringeinrichtungen zur Verfügung gestellt. Zur besseren Abdeckung von Bioziden im Oberflächengewässer-Monitoring wird die Zusammenarbeit mit den Bundesländern, die das Wasserrahmenrichtlinien-Monitoring umsetzen, empfohlen. Um auch eine retrospektive Verfolgung von Änderungen zu erlauben, wird die Nutzung von Proben aus Umweltprobenbanken vorgeschlagen. Archivierte Biota Proben (z.B. Fisch- oder Greifvogelgewebe) können verwendet werden, um Trends unpolarer Biozide zu identifizieren. Polare Stoffe können in archivierten Schwebstoffproben aus Flüssen analysiert werden (Beispiele liegen vor). Spezielle Aspekte können in einem Schnappschussmonitoring untersucht werden (z.B. Antifouling-Wirkstoffe in Marinas). Für das Bodenmonitoring wird die Zusammenarbeit mit Bundesländern, die Bodendauerbeobachtungsflächen betreiben, empfohlen. Hier erscheinen Forschungsprojekte als am besten geeignet, beispielsweise zur Untersuchung von Bioziden auf Flächen, die mit Gülle oder Klärschlamm beaufschlagt wurden.

Abstract

The Biocidal Product Regulation (No. 528/2012) causes changes of the use of biocides and consequently of their environmental concentrations. For biocides included in the list of approved substances levels may increase while decreasing environmental burdens are expected for substances with non-approval decisions or implemented risk mitigation measures. Such consequences may be proven by an environmental monitoring. The data would also allow checking whether the concentrations are above derived no-effect levels. However, in most monitoring programmes biocides are not appropriately covered. Traditionally, e.g., in surface waters mainly plant protection products (partly also approved as biocides), compounds from industrial sources and legacy chemicals are monitored. This project aims to propose a comprehensive monitoring concept for biocides. Main purpose of this approach is to achieve a better coverage of biocides in existing monitoring programmes. As a first step, relevant compartments were identified and relevant biocides prioritised. These lists can be provided to monitoring authorities. For the better coverage of biocides in surface water monitoring, cooperation with the German federal states which operate the Water Framework Directive monitoring is recommended. To allow also a retrospective tracking of changes, the utilisation of samples from existing specimen banks is suggested. Archived biota samples (e.g., fish or raptor tissues) may be used to identify trends of non-polar biocides. For more polar compounds archived suspended particulate matter from rivers may be analysed (examples already available). Special aspects may be investigated in a snapshot monitoring (e.g., antifoulants in marinas). For soil monitoring, cooperation with federal states which operate permanent soil investigation sites is recommended. In this area research projects seem most appropriate, for example for investigating biocides on sites with liquid manure or sewage sludge spreading.

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Abbreviations

AA	annual average
BAuA	Federal Institute for Occupational Safety and Health (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin)
BCF	bioconcentration factor, determined as L/kg (partly given without a unit)
BIT	1,2-benzisothiazoline-3(2H)-one
BPD	Biocides Product Directive (Directive 98/8/EC of the European Parliament and of the Council on the placing on the market of biocidal products)
BPR	Biocides Product Regulation (Regulation No. 528/2012 of the European Parliament and of the Council concerning the making available on the market and use of biocidal products; replaced the BPD by September 2013)
BVL	Federal Office of Consumer Protection and Food Safety (Bundesamt für Verbraucherschutz und Lebensmittelsicherheit)
CAS no.	international denomination system for chemicals (CAS = Chemical Abstracts Service)
DCOIT	4,5-dichloro-2-octyl-2H-isothiazol-3-one
DMSA	N,N-dimethyl-N'-phenylsulfamide (dichlofluanid TP)
EINECS Nr.	specific denomination for chemicals in the European Inventory of Existing Commercial Chemical Substances
ESD	emission scenario document
EQS	environmental quality standard
ESB	environmental specimen bank
EU	European Union
GC-MS	gas chromatography with a mass spectrometer as detector
GUS	Groundwater Ubiquity Score
HPLC-MS	high performance liquid chromatography with a mass spectrometer as detector
IME	Institute for Molecular Biology and Applied Ecology (Fraunhofer IME)
IPBC	3-iodo-2-propynylbutylcarbamate
K_{OC}	partition coefficient organic carbon/water
K_{OW}	partition coefficient n-octanol/water
LANUV	environmental authority for the German federal state of North Rhine Westphalia (Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen)
LAWA	working group of German federal states and the federal government in the field of water monitoring (Bund/Länder-Arbeitsgemeinschaft Wasser)
LfU	environmental authority for the German federal state of Bavaria (Bayerisches Landesamt für Umwelt)
LOD	limit of detection
log	decadic logarithm

LOQ	limit of quantification
LUBW	environmental authority for the German federal state of Baden-Wuerttemberg (Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg)
MAC	maximum allowable concentration
MIT	2-methyl-4-isothiazolin-3-one
MITC	Methylisothiocyanate (dazomet TP)
MS	mass spectrometry
OGewV	German Surface Water Ordinance (Oberflächengewässerverordnung)
PBT	persistent, bioaccumulating, toxic (according to certain criteria)
PEC	predicted environmental concentration
PNEC	predicted no effect concentration
PPP	plant protection product
PT	product type of biocides
QAC	quaternary ammonium compounds
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SGAR	second-generation anticoagulant rodenticide
SPM	suspended particulate matter
STP	sewage treatment plant
TBT	tributyltin
TNsG	Technical Notes for Guidance
TP	transformation product
UBA	German Federal Environment Agency (Umweltbundesamt)
vB	very bioaccumulative (according to certain criteria)
vP	very persistent (according to certain criteria)
WFD	Water Framework Directive

Statement on data

All data were carefully compiled and checked. However, it cannot be excluded that errors may have occurred.

Decisions on approval/non-approval according to BPD/BPR of biocides use for certain product types (PT) taken before April 2014 were considered. A non-approval decision for a PT may change the assessment of the respective biocide (prioritisation for monitoring).

1 Identification of relevant matrices

In the context of this project an environmental monitoring is understood as a monitoring at a regional or national scale (but it is not intended to investigate possible local effects of a biocide application; see also section 4.1). The intention is to identify changes of use patterns of biocides following the implementation of the European Biocidal Product Directive 98/8/EC on placing biocidal products on the market (BPD; EC 1998) and the EU Biocidal Product Regulation No 528/2012 (BPR, EU 2012; to be applied since September 1, 2013). These changes should have effects on environmental concentrations of substances. For biocides which are included in the positive list (BPD: Annex I/Ia; BPR: list of approved substances) concentrations may increase. On the opposite, lower environmental burdens are expected for substances which are retrieved from the market as consequence of BPD/BPR non-inclusion decisions.

Another motivation of a biocide monitoring could be to compare measured environmental concentrations with the predicted environmental concentrations (PEC) derived during risk assessment. This may identify gaps in the assessment. A monitoring could also be used to verify that risk mitigation measures that were implemented during the process of inclusion/approval of active substances for the BPD/BPR list of approved substances are successful.

Since several substances used as active ingredients in biocidal products are also used under further regulations (e.g., as plant protection products or pharmaceuticals) it has to be evaluated whether the source of possible findings can be clearly allocated (i.e. to the use of a biocidal product). A pragmatic approach is to initially focus on those compounds (and transformation products) only used as biocides or to choose conditions which - with a certain probability - exclude other sources beside biocide application.

As a basis for the subsequent prioritisation of biocides for an environmental monitoring the relevant environmental compartments have to be identified. The evaluation follows the approach of a previous study (Rüdel and Knopf 2012) where relevant compartments (water, soil, air) were assessed with regard to their relevance for monitoring. The evaluation used on the one hand information from a study conducted for the EU commission on the environmental relevance of the different biocide product types (PT) for emissions to environmental media (COWI 2009). On the other hand, information from monitoring studies retrieved from peer-reviewed papers and internet-published reports (see compilation, work package II) is used as a basis for selection.

The study by COWI (2009) evaluated the possible environmental impact through the use of biocides depending on the application (i.e. PT) and the user category (e.g. application by professional or non-professional users). It was differentiated between potential environmental impacts of the environmental media in the application phase (usually short) and the service life (usage) phase (usually much longer than the application phase).

Table 1 shows the aggregated results of the qualitative assessments for each PT for direct and indirect environmental inputs of biocides from application and service life phase by COWI (2009). This approach was discussed in detail in the previous study (Rüdel and Knopf 2012).

Table 1: Overview of overall tonnage estimates and significance of direct and indirect environmental inputs related to the use phase of biocides (per PT). The table was adapted on basis of the expertise of the UBA (changed fields are shaded). The specific exposure assessments do not consider the overall tonnages.
Source: extracted from Table 4-10 in COWI 2009; the PT numbers were adapted to those applied in regulation EU 528/2012 (EU 2012). STPs - sewage treatment plants; XXX - high relevance; XX - medium relevance; X - low relevance; (-) - probably not relevant.

Product type no.	Product type description	Tonnage (annual)	Direct environmental exposure	Indirect environmental exposure via STPs
Main Group 1: Disinfectants				
PT 1	Human hygiene	XXX	(-)	XX
PT 2	Disinfectants and algaecides not intended for direct application to humans or animals	XXX	X	XXX
PT 3	Veterinary and hygiene	XXX	X	XX
PT 4	Food and feed area	XXX	(-)	XXX
PT 5	Drinking water	XXX	X	X
Main group 2: Preservatives				
PT 6	Preservatives for products during storage	XX	X	X
PT 7	Film preservatives	XX	XX	XX
PT 8	Wood preservatives	XXX	XX/XXX	X
PT 9	Fibre, leather, rubber, and polymerised materials preservatives	XX	X	X
PT 10	Construction material preservatives	XXX	XX	XX
PT 11	Preservatives for liquid cooling and processing systems	XXX	XX	XX
PT 12	Slimicides	XX	XX	XX
PT 13	Working or cutting fluid preservatives	XX	-	X
Main Group 3: Pest control				
PT 14	Rodenticides	X	XX	X
PT 15	Avicides§	(-)	XX	(-)
PT 16	Molluscicides, vermicides and products to control	(-)	XXX	(-)

Product type no.	Product type description	Tonnage (annual)	Direct environmental exposure	Indirect environmental exposure via STPs
	other invertebrates #			
PT 17	Piscicides §	(-)	XXX	(-)
PT 18	Insecticides, acaricides and products to control other arthropods	XXX	XXX	XXX
PT 19	Repellents and attractants	XX	XX	XX
PT 20	Control of other verte-brates §	(-)	XX	(-)
Main Group 4: Other biocidal products				
PT 21	Antifouling products	X	XXX	(-)/X
PT 22	Embalming and taxidermist fluids	X	X	X

no biocide in the review programme for this PT. § no authorisation in Germany for this PT.

However, the classification in Table 1 has been adjusted to reflect the experience of the German Federal Environment Agency (UBA). For example, it seems that potentially sewage-related PTs (e.g., PT 8, 10, 18, 19) were not considered appropriately in the COWI (2009) study as they were assessed as "not relevant for environmental inputs via sewage treatment plants (STPs)". While the relevance of this aspect was identified for the application phase for these four PTs in COWI (2009), the assessment for the service life phase did not reveal any relevance for STP emissions (or only a low relevance in case of PT 19). As the use phase was apparently more heavily weighted, these PTs as a whole have been classified as non-relevant for emissions to STPs by COWI (2009). However, based on the expertise of UBA in this field additional PTs were assessed as relevant (changed assessments are shaded in Table 1).

In the context of this project all PTs in the table above are classified as relevant which are assigned to either high (XXX) or medium (XX) relevance for the respective path (direct, indirect). With regard to the inputs into soils it is noted that in the COWI (2009) study there was no differentiation between direct and indirect inputs. Indirect exposures into soils may be relevant for PT 3 biocides upon agricultural slurry application. The indirect contamination of soils by agricultural use of sewage sludge is also not explicitly discussed in the report by COWI (2009).

The COWI assessment results are similar to those from other studies. Kahle and Nöh (2009) assessed particular antifouling products (PT 21), preservatives for liquid-cooling systems (PT 11) and biocides leached by and collected in rainwater (e.g. masonry preservatives, PT 10) as relevant regarding direct biocides inputs into surface waters. Direct entries of biocides into surface waters by rain water are also possible since about 40% of the sewers are operated with separator systems. For mixed sewer system overflows may occur by stormwater causing (biocides containing) sewage to be discharged to surface waters without treatment. The relevance of façade preservatives leaching was recently shown in a number of studies (e.g., Burkhardt et al. 2012; see also workshop report Jäger et al. 2013). Also the use of rodenticides (PT 14) in sewers may cause direct inputs into surface waters either through rainwater or via stormwater overflows (Kahle and Nöh 2009).

In recent years there has also been evidence from investigations in, e.g., the UK and Denmark on rodenticides burdens of rodents and/or predators that feed on them (Tosh et al. 2012; Christensen et al. 2012; Hughes et al. 2013; Norström et al. 2013). Feral animals (rodents, raptors) often contained residues of second generation anticoagulant rodenticides (SGAR). These are environmentally relevant because they potentially fulfill PBT (persistent, bioaccumulative, toxic) and vPvB (very bioaccumulative, very persistent) criteria and may cause unacceptable risks in terms of primary and secondary poisoning of predators. Due to infection prevention and health care reasons they are nevertheless included in the list of approved substances of the BPD/BPR, but only for a shorter period of five years. Especially for these compounds an environmental monitoring seems appropriate to document the current residues levels and to verify the effectiveness of the mitigation measures.

In the report on work package III of the current project a summary was prepared on findings of biocides in relevant compartments in relation to product types (Table 2; based on the results of a survey of monitoring institutions in Germany and a literature search; Rüdel and Fliedner 2014, updated and amended from Rüdel and Knopf 2012).

Table 2: Product types (PTs) relevant for a biocide monitoring and their importance for environmental compartments. Examples are given for compounds already detected in the environment. Summary based on the results of a survey of monitoring institutions in Germany and a literature search (Rüdel and Fliedner 2014, updated and amended from Rüdel and Knopf 2012).
X - only single data/reports, no systematic monitoring; XX - data base for several compounds; XXX - good data base for many biocides, systematic monitoring;
(-) - no relevant data/reports.
PTs are assigned according to BPR (EU 528/2012, EU 2012).

Matrix	Relevant product types	Important for the compartment according to monitoring data	examples for detected compounds / concentrations > LOQ
Surface waters - marine (marinas/coastal waters)	PT 11, 12, 21	XX	Diuron§#, cybutryne, dichlofluanid§#, chlorothalonil§#, DCOIT
Sediments- marine (marinas/coastal waters)	PT 11, 12, 21	XX	Cybutryne, dichlofluanid§#, chlorothalonil§#
Aquatic organisms - marine (marinas/coastal waters)	PT 11, 12, 21	X	Cybutryne
Surface waters - limnic (direct input)	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21	XXX	Carbendazim#, diuron#, DEET, diazinon§, cybutryne, tebuconazole#
SPM - limnic	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21	X	QAC, triclosan and TP methyl-triclosan
Sediments - limnic	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21	X	Cybutryne, triclosan

Matrix	Relevant product types	Important for the compartment according to monitoring data	examples for detected compounds / concentrations › LOQ
Aquatic organisms - limnic	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21	X	Triclosan and TP methyl-triclosan
STP effluents	PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19	X	Diuron#, thiabendazole#, triclosan and TP methyltriclosan, isoproturon#, propiconazole#, bromadiolone, difenacoum#
Sewage sludge (relevant for indirect inputs into soil)	PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19	X	BIT, clorophene, imazalil#, cybutryne§
Soil (direct input)	PT 7, 8, 10, 14, 18, 19	-	-
Ground water	PT 7, 8, 10, 14, 18, 19	XX	Propiconazole#, terbutryn
Soil organisms (e.g., earth worms)	PT 7, 8, 10, 14, 18, 19	-	-
Terrestrial organisms, feeding on soil organisms, near to buildings/developments (e.g., rodents, raptors)	PT 14	X	Difenacoum#, bromadiolon# coumatetralyl#, brodifacoum#
Atmosphere	PA 8, 11, 14, 18	-	Triclosan§
Slurry (relevant for indirect inputs into soil)	PA 3, 18	-	-
Other matrices: compost, digestate	*	(X)	Imazalil#, thiabendazole#, tebuconazole#

also authorised as PPP at the time of the investigation. § currently no authorisation for a PT which is relevant for the respective matrix. $ see also further PTs that are relevant for indirect inputs in surface water via STP effluents or indirect inputs into soil via sewage sludge or slurry. * residues are probably from PPP treatments of applied organic material.

Passive samplers are excluded here because up to now no relevant routine monitoring activity is performed with these devices. Related to biocides monitoring only one study was identified using passive samplers (Vermeirssen et al. 2009) which, however, reports only amounts of substances per sampler but no concentrations. Thus a compliance monitoring with regard to environmental quality standards or PNECs is not directly possible. Data on amounts of substances per sampler are in principle sufficient for a trend monitoring but this approach seems currently less relevant. Further information on passive sampling is provided in a position paper of the NORMAN "Expert Group on Passive Sampling" (Vrana et al. 2010). In the context of the NORMAN network also an international intercalibration study on passive sampling was organised in collaboration with the Joint Research Centre of the European Commission. The exercise was evaluated during a workshop in 2011 (www.norman-network.net/?q=node/101; a report is not yet available). An expert meeting organised by the NORMAN network in 2013 dealt with linking of environmental quality standards and passive sampling (www.norman-network.net/?q=node/124).

2 Analytical methods

In principal for each biocidal product and each active substance the registrant has to provide analytical methods for the products (e.g., for determining the amount of active ingredients in formulations) and for relevant matrices (including environmental matrices, e.g., water or soil in case an occurrence of the compounds in the medium can be expected). In the context of the BPD (98/8/EC, EC 1998), the requirements for the analytical methods were described in the “Guidance on data requirements for active substances and biocidal products” (ECB 2008) and in Technical Notes for Guidance (TNsG 2009). An updated version for use with the BPR (EU 528/2012, EU 2012) was provided recently (“Guidance on information requirements”, ECHA 2013).

However, the analytical methods are only described briefly in the publicly available EU Doc I biocide Assessment Reports. Detailed information is only provided in not publicly available annexes.

In cases where biocides are also authorised as plant protection products (PPP), additional information may be gained from the PPP Assessment Reports. Requirements for methods provided by manufacturers for the post-registration monitoring of PPP are described in the “Guidance document on pesticide residue analytical methods (SANCO/825/00 rev. 8.1; SANCO 2010). Residue analytical methods for PPP are available from national competent authorities (in Germany the Federal Office of Consumer Protection and Food Safety, BVL). In some cases also national or international standard methods are available (e.g., for isoproturon in waters, EN ISO 11369 1997).

Especially in the case of surface water monitoring analytical methods for a number of relevant biocides are available in the open literature. Often these are multi-methods which allow the coverage of several substances (e.g., Wick et al. (2010) for biocides in sewage sludge or Walker et al. 2008 for SGAR in raptor tissue). However, in some cases the possibility to cover numerous substances is traded off against a lower sensitivity for some of the covered compounds (i.e. methods optimised for single substances have often significantly lower limits of quantification).

Important aspects of the analytical methods are:

- Limit of Detection (LOD): the LOD is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidence limit (e.g., 1%); at concentrations above the LOD, detection of the target compound is possible, but the analytical value is uncertain so that in the range between LOD and Limit of Quantification (LOQ) only qualitative data can be determined.
  According to EU directive 2009/90/EC (EC 2009a) “limit of detection” means the output signal or concentration value above which it can be affirmed, with a stated level of confidence, that a sample is different from a blank sample containing no determinant of interest.
- Limit of Quantification (LOQ): the LOQ is the lowest actual amount of an analyte that can be reliably detected; only above the LOQ a quantitative value can be reported.
  According to EU directive 2009/90/EC (EC 2009a) “limit of quantification” means a stated multiple of the LOD at a concentration of the determinant that can reasonably be determined with an acceptable level of accuracy and precision; the LOQ can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank.
  Often the LOQ is calculated as 3 * LOD.

- Accuracy: the accuracy of an analytical method expresses the closeness of agreement between the value which is accepted either as a conventional true value or an accepted reference value and the value found (TNsG 2009).
- Recovery: the amount measured as a percentage of the amount of analyte(s) (active substance and relevant metabolites/transformation products) originally added to a sample of the appropriate matrix which contains either no detectable level of the analyte or a known detectable level. Recovery experiments provide information on both precision and trueness (bias), and thereby the accuracy of the method (TNsG 2009).
- Precision: the precision of an analytical method expresses the closeness of agreement between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions (TNsG 2009).
- Selectivity (Specificity): selectivity refers to the extent to which the method can be used to determine particular analytes in mixtures or matrices without interferences like impurities, metabolites/transformation products, matrix etc. (TNsG 2009).
- Calibration: refers to the ability of a detection system to produce an acceptable well defined correlation between the instrumental response and the concentration of the analyte in the sample. The analyte concentration to be measured should be within the defined dynamic range of the instrument (TNsG 2009).
- Repeatability: refers to the closeness of agreement between mutually independent test results obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time (TNsG 2009).
- Reproducibility: refers to the closeness of agreement between independent results obtained with the same method on identical test material obtained but under different conditions (e.g., within-laboratory or intra-laboratory reproducibility; TNsG 2009).

The EU directive 2009/90/EC (Quality Assurance/Quality Control Directive; EC 2009a) on technical specifications for chemical analysis and monitoring of water status covers further important aspects which are also applicable to monitoring of other media:

- Minimum performance criteria for methods of analysis: the minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50% or below (with a coverage factor of $k = 2$) which is estimated at the level of relevant environmental quality standards and a LOQ equal or below a value of 30% of the relevant environmental quality standards; in this context "uncertainty of measurement" means a non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand, based on the information used.
- Mean value calculation: if the concentration of a chemical in a given sample is below the LOQ, the measurement results shall be set to half of the value of the LOQ concerned for the calculation of mean values. Where a calculated mean value of the measurement results in a value below the LOQ, the value shall be referred to as "less than LOQ".
- Quality assurance and control: according to EU directive 2009/90/EC (EC 2009a) laboratories should apply a quality management system in accordance with the international standard EN ISO/IEC 17025 or other equivalent standards accepted at international level; the compliance with the standard should be demonstrated by analysis of available reference materials that are representative of the analysed samples and by participation in proficiency testing programmes covering the respective methods of analysis.

If possible, hyphenated mass spectrometric analytical methods should be applied (e.g., GC-MS or HPLC-MS). These allow the mass spectrometric confirmation of the presence of organic target compounds. Mass spectrometry in conjunction with chromatographic separation is a powerful tool for identification since it simultaneously provides a chromatographic retention time, an ion mass/charge ratio, and concentration data (SANCO/12495/2011, SANCO 2011; contains further guidance on analysis like identification requirements for different types of mass spectrometers and maximum permitted tolerances for relative ion intensities for different mass spectrometry techniques). Due to the different substance classes and properties of biocides often a complementary usage of GC-MS and HPLC-MS methods will be required (see also conclusions from the workshop on biocides monitoring in 2012; workshop report, Jäger et al. 2013).

For the analytical methods appropriate standards have to be applied. For many compounds unlabelled standards are available (especially for those biocides which are also used as pesticides). Examples for distributors are Sigma-Aldrich (PESTANAL products, www.sigmaaldrich.com), LGC Standards (www.lgcstandards.com, distributes also, e.g., products from Cambridge Isotope Laboratories, Inc.), or BIOZOL Diagnostica Vertrieb GmbH (www.biozol.de). However, for a reliable and accurate analysis (especially in complex matrices like biota, sediment or sewage sludge) isotopically labelled standards are required (e.g., Deuterium or ^{13}carbon-labelled). The lack of labelled standards for many of the relevant biocides has been identified as a major hindrance during the workshop on biocides monitoring in 2012 (workshop report, Jäger et al. 2013). Workshop participants recommended the joint acquisition of custom-synthesised isotopically labelled substances for the most important candidates for biocides monitoring.

The following data should at least be reported (minimum set, modified from Egli et al. 2003):

- Sample: adequate description of the sampling site location (geo-coordinates), information on frequency of sampling and sampling data, description of the sampling method, size of samples, storage conditions after sampling until analysis, storage duration, information if blank samples were taken in the field;
- Analytical method: description of method and required equipment, information on applied calibration procedure (e.g., external standards, internal standard method, use of isotopically labelled standards; number and concentration of calibration points), quantitation procedure (e.g., selected mass fragments for mass spectrometric analysis), method validation summary (including at least LOD, LOQ, recovery from spiked samples, blank values, repeatability), quality assurance measures (e.g., stability and recovery tests), clear statement on result units and basis (e.g., dry weight, wet weight) and possible normalisations (e.g., on lipid weight for biota, on total organic carbon content for sediments);
- Sample analysis: pre-treatment before analysis (e.g., filtration, drying conditions if appropriate, sieving conditions for soil or sediments), information on sample homogenisation and subsampling (if appropriate), information on measurement of replicates, measurement uncertainty.

3 Principal aspects of trend monitoring

3.1 Trend monitoring requirements

One important aspect regarding the analytical method is whether the expected concentrations can be determined with the required quality. Therefore the limit of detection (LOD) and limit of quantification (LOQ) should be known. Another important aspect is the method precision (operationalised as standard deviation for replicate measurements) in the range of the concentrations expected in the monitoring study.

For a trend monitoring it has to be clarified whether the expected changes are principally detectable. This depends on different factors. To illustrate the different aspects the programme TRENDS (Gerrodette and Brandon 2006; TRENDS version 3.0; Southwest Fisheries Science Center, La Jolla, California, USA) was applied. TRENDS is designed to carry out a power analysis of linear regression. It summarises the power analysis in five parameters (TRENDS User's Guide; Gerrodette 1993):

- duration of study,
- rate of change,
- precision of analytical method,
- α (type 1 error rate), and
- power (1 - β, where β is the type 2 error rate).

The value of any one of these can be estimated if the other four are specified. The relationship between these parameters is affected by other aspects, such as whether the change is linear or exponential, whether the change is positive or negative, whether the statistical test is one- or two-sided (this depends on the expectation of a certain direction of a trend; a two-sided test is applied if the trend direction is not clear), and how the precision of the estimates depends on the target substance concentration (TRENDS User's Guide, Gerrodette 1993). The TRENDS tool allows the answering of questions such as: How many years are required to detect a trend? How large is the rate of change that can be detected? What is the probability of detecting a trend in dependence of the measurement accuracy?

α is the probability of a Type I error in any hypothesis test (i.e. an incorrectly claiming of statistical significance). β is the probability of Type II error in any hypothesis test (i.e. an incorrectly concluding that no statistical significance exists). The power or sensitivity (calculated as 1 - β) of a statistical test is the probability that the test will reject the null hypothesis when the null hypothesis is false. As the power increases, the chances decrease that a Type II error occurs.

Usually an α of 0.05 or 0.1 is applied and a β of 2 * α. Table 3 and Table 4 give overviews of the probability of a trend detection depending on different parameters (for an assumed linear or exponential change of annual concentration values). A screen shot of the programme TRENDS is shown in Figure 1.

Table 3: Probability of trend detection (power) depending on different parameters. Fixed parameters: one annual sampling, linear trend, one-sided test (decrease or increase of concentration of target substance expected), precision is correlated to square root of concentration (i.e. the measurement uncertainty is higher at lower concentrations). The power for each scenario was calculated with the TRENDS programme (Gerrodette and Brandon 2006). An α of 0.05 or 0.1 was applied and a β of 2 * α.

Monitoring period (years)	rate of change (% per year)	Method precision for initial concentration (%)	α (Type 1 error rate)	power (1 - **β**, **β** = Type 2 error rate)	Comment#
4	+10	20	0.1	0.33	Not sufficient
4	+10	10	0.1	0.63	Not sufficient
5	+10	20	0.1	0.48	Not sufficient
7	+10	15	0.1	0.94	
7	+10	20	0.1	0.80	
7	+10	30	0.1	0.55	Not sufficient
4	+15	10	0.1	0.85	

Monitoring period (years)	rate of change (% per year)	Method precision for initial concentration (%)	α (Type 1 error rate)	power (1 - β, β = Type 2 error rate)	Comment#
5	+25	20	0.1	0.92	
7	+5	20	0.1	0.44	Not sufficient
4	-10	20	0.1	0.38	Not sufficient
4	-10	10	0.1	0.72	Not sufficient
5	-10	20	0.1	0.59	Not sufficient
7	-10	15	0.1	1.0	
7	-10	20	0.1	0.94	
7	-10	30	0.1	0.74	Not sufficient
4	-15	10	0.1	0.94	
5	-25	20	0.1	1.0	
7	-5	20	0.1	0.51	Not sufficient
7	+10	15	0.05	0.84	Not sufficient
7	+10	20	0.05	0.64	Not sufficient
7	+20	20	0.05	0.97	
7	-10	15	0.05	0.97	
7	-10	20	0.05	0.85	Not sufficient
7	-20	20	0.05	1.0	

not sufficient if the power is below 0.8 (for α = 0.1) or 0.9 (for α = 0.05).

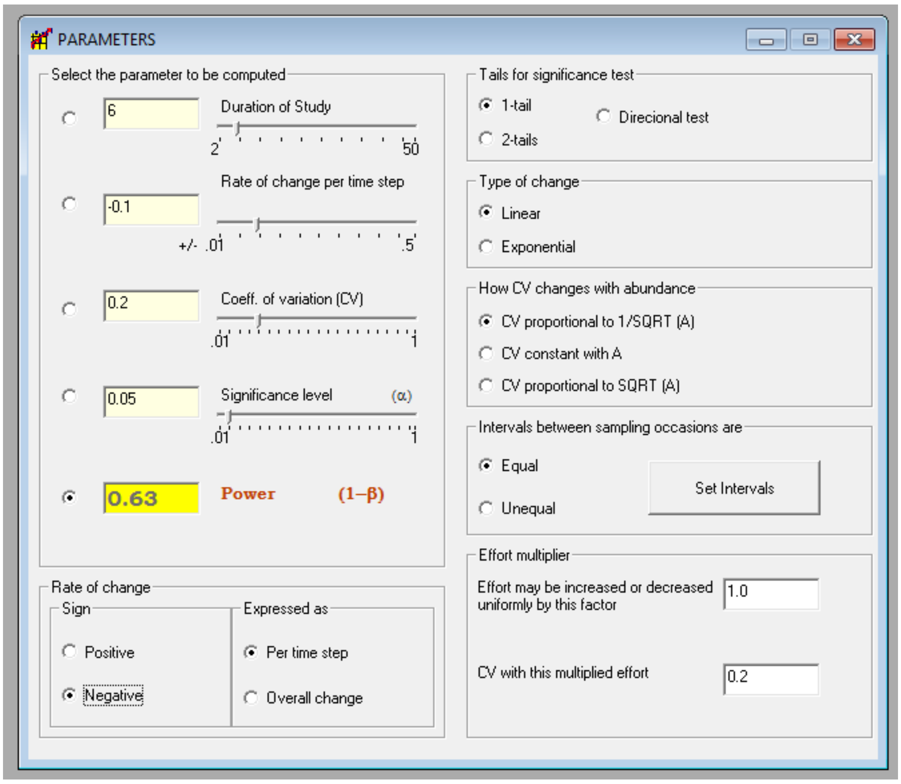
Table 4: Probability of trend detection (power) depending on different parameters. Fixed parameters: one annual sampling, exponential trend, one-sided test (decrease or increase of concentration of target substance expected), precision is correlated to square root of concentration (i.e. the measurement uncertainty is higher at lower concentrations). The power for each scenario was calculated with the TRENDS programme (Gerrodette and Brandon 2006). An α of 0.05 or 0.1 was applied and a β of 2 * α.

Monitoring period (years)	rate of change (% per year)	Method precision for initial concentration (%)	α (Type 1 error rate)	power (1 - β, β = Type 2 error rate)	Comment#
4	+10	20	0.1	0.36	Not sufficient
4	+10	10	0.1	0.69	Not sufficient
5	+10	20	0.1	0.56	Not sufficient
7	+10	15	0.1	0.99	
7	+10	20	0.1	0.91	

Monitoring period (years)	rate of change (% per year)	Method precision for initial concentration (%)	α (Type 1 error rate)	power (1 - β, β = Type 2 error rate)	Comment#
7	+10	30	0.1	0.69	Not sufficient
4	+15	10	0.1	0.91	
5	+25	20	0.1	0.99	
7	+5	20	0.1	0.50	Not sufficient
4	-10	20	0.1	0.34	Not sufficient
4	-10	10	0.1	0.66	Not sufficient
5	-10	20	0.1	0.50	Not sufficient
7	-10	15	0.1	0.94	
7	-10	20	0.1	0.81	
7	-10	30	0.1	0.58	Not sufficient
4	-15	10	0.1	0.87	
5	-25	20	0.1	0.93	
7	-5	20	0.1	0.45	Not sufficient
7	+10	15	0.05	0.95	
7	+10	20	0.05	0.80	Not sufficient
7	+20	20	0.05	1.00	
7	-10	15	0.05	0.85	Not sufficient
7	-10	20	0.05	0.65	Not sufficient
7	-20	20	0.05	0.96	

not sufficient if the power is below 0.8 (for α = 0.1) or 0.9 (for α = 0.05).

Figure 1: Screen-shot of the operating surface of the TRENDS programme (Gerrodette and Brandon 2006). The power (1 – β) of a specific monitoring scenario is calculated depending on four other parameters: duration of study, expected rate of change, estimated precision of analytical method (as coefficient of variation), and significance level (α, Type 1 error rate).



3.2 Trend evaluation tools

For the evaluation of trend monitoring studies several tools are available. The applicability depends, for example, on the quality of the data and the length of the time series.

A first approach could be the testing for a trend by linear regression analysis. This procedure is the standard approach according to Appendix 11 of the German surface water ordinance (OGewV 2011).

Another standard approach for the evaluation of a trend monitoring data set is the application of the two-sided non-parametric Mann-Kendall test. For this test, for example, a Microsoft Excel tool developed by Salmi et al. (2002) is available. As output, the significance level of the respective trend is received.

Time series may also be evaluated by applying a robust regression-based analysis to detect possible trends in the datasets (Nicholson et al. 1998). A statistical tool for this methodology may be retrieved from the Arctic Monitoring and Assessment Programme homepage (Bignert 2007). The applied log-linear regression analysis yields a slope of the line which describes the annual concentration change as percent value. If a trend is detected, the actual probability (p value) is given.

Recently at the UBA a new tool was developed (LOESS-Trend, Version 1.0, based on Microsoft Excel; UBA 2013). This tool fits a locally weighted scatterplot smoother (LOESS, with a fixed window width of 7 years) through the yearly concentration data. Then it tests for significance of linear and non-linear trend components by means of an Analysis of Variance (ANOVA) following the approach of Fryer and Nicholson (1999). The assessment is based on the original data (no log transformation) for matters of graphic vividness. The LOESS-Trend tool also allows the evaluation of the significance of differences in concentration levels between selected years (contrast) by means of a t-test.

3.3 Data considerations

For a sound statistical evaluation of a trend about seven data points (here assumed: annual data) are required. With a reasonable method precision of about 20% an annual concentration change of 10% is detectable at an α of 0.1 with a probability of 80% (power of 0.8) as increase or with a probability of 94% (power of 0.94) as decrease (see section 3.1). A higher annual change or a better method precision would enhance the power.

In a shorter period of about 4 - 5 years only higher annual changes could be detected (e.g., in 5 years a 25% decrease with a method precision of 20% and an α of 0.1 with a probability of 100%; for the respective increase the power for trend detection would be 0.92). Such changes could occur if emissions change rapidly. For example, in a study by Rüdel et al. (2012) a significant annual decrease of 48% of the concentrations of the brominated flame retardant hexabromocyclododecane (HBCD; sum of three diastereomers) in bream from the river Rhone was detected in the period 2007 - 2010 (trend detected by log-linear regression analysis based on the PIA tool by Bignert 2007). It is assumed that the decrease was caused by the implementation of emission control measures during the production and processing of HBCD. Similar changes can be expected if, e.g., certain biocides are no longer marketable after a non-inclusion decision into the list of approved substances under the EU biocide regulations (BPD/BPR) was taken.

4 Biocide monitoring scenarios

4.1 General

In this chapter scenarios for a biocides monitoring are proposed for the most relevant compartments. Data are structured according to matrix, relevant product types and typical substances, the suggested monitoring approach, the availability of appropriate analytical methods (standard methods, provided in biocide/PPP assessment reports, or literature protocols), and literature findings and/or reports on programmes in Germany or other European countries.

A monitoring may be conducted at different scales regarding time and space. Here four different approaches are considered (it is assumed that an appropriate analytical method is applied for which the limit of quantification is in a relevant range, e.g., that it allows to test whether a known effect concentration like a PNEC is exceeded):

- Research projects: special investigations on one or a few compounds at one or a few sampling sites; for example, performance of a high number of measurements within a short period to characterise emission patterns or development of an appropriate analytical method for the target compound(s).
- Screening (or snapshot monitoring): a screening for one or more target compounds may be performed with one or a few sampling time points and a limited number of sampling sites (local to regional scale); it may be performed to test whether a specific chemical can be detected in an environmental compartment; from screening data it can mainly be concluded whether a target compound is consistently detectable in the selected investigated compartment (feasibility study).
- Survey: a survey may be performed with one or a few sampling time points to get data on the concentrations of one or more target compounds in an environmental compartment; a survey may cover a larger number of sampling sites so that the resulting data can be assumed to be representative (regional to national scale); survey data allow a conclusion on the relevance of

the target compounds for the investigated compartment; moreover, a spatial comparison is possible.
- Routine monitoring: a routine monitoring is assumed to be performed on a national scale and covers ideally all relevant target compounds in an environmental compartment; a routine monitoring is performed over a longer period (e.g., > 5 years) and allows the detection of temporal trends in the concentration data; furthermore a spatial comparison is possible.

Table 5 presents an overview on the characteristics of the monitoring approaches with regard to number of compounds, geographical scale and sampling period. Retrospective monitoring studies with archived samples (e.g., provided by the German ESB) may be classified as routine monitoring (if longer times series of standardised sampled material are analysed to detect possible temporal trends of environmental burdens).

Table 5: Overview of monitoring approaches (approximate numbers for selected criteria).

Monitoring approach	Number of compounds covered	Number of sampling sites	Number of sampling events
Research projects (short period)	1 – 3	1 – 3	1 – > 10
Screening (short period)	1 – 9	3 – 9	1 – 5
Survey (limited period)	1 – > 10	> 10	1 – 9
Routine monitoring (permanent)	All relevant compounds	Coverage of representative sites	Not limited; frequency: monthly – annually

A further consideration especially for a biocides monitoring is whether the selected target compounds are also used under other regulations, e.g., as plant protection product (PPP), veterinary or human pharmaceutical or industrial chemical regulated under the REACH Regulation. If a compound is used under different regulations it has to be evaluated whether possible findings can be clearly allocated to one source (e.g., biocide use or PPP use). In an investigation in Switzerland it could be demonstrated that a source allocation is possible in a small area (Wittmer et al. 2011; see also section 4.6). However, the approach required a parallel measurement of surface water, stormwater and sewage samples and was accompanied by a survey of the use of biocides and PPP in households and agriculture.

For a larger scale monitoring pragmatic choices may help to minimise the contribution from one or the other source (e.g., by discrimination in time or space). For instance, analyses of surface water samples from larger rivers in winter may reflect the levels of the biocide use of a compound which is also used as PPP; or concentrations in sewage treatment plants fed with sewage from an urban region probably reflect mainly the biocidal use of such a dual use compound. This may be more difficult for compounds used as pharmaceuticals and biocides because the usage pattern may overlap widely (e.g., both disinfectants and pharmaceuticals are discharged via wastewater to sewage treatment plants).

4.2 Monitoring of raptors

Most rodenticides potentially have PBT properties (persistent, bioaccumulative, toxic) and may cause secondary poisoning of predators by prey which has taken up active ingredients from baits exhibited near buildings or developments. This has already been demonstrated in studies in, e.g., the UK or Denmark (e.g., Christensen et al. 2012; Walker et al. 2012; Hughes et al. 2013). In Norway, the second-generation anticoagulant rodenticides (SGARs) brodifacoum, bromadiolone, difenacoum and flocoumafen were detected in 70% of golden eagle and 50% of eagle owl livers at concentration in the range 11 - 255 ng/g wet weight (sum SGARs; Langford et al. 2013).

A screening on pollutants in abandoned peregrine falcon eggs was performed in the federal state of Baden-Württemberg in the years 2009 and 2010 (personal communication: K.T. von der Trenck, LUBW; von der Trenck 2012). The study comprised also nine pesticides, including bifenthrin (PT 8, also PPP until 2011), esfenvalerate (PT 18, also PPP), brodifacoum (PT 14, also PPP until 2010) and difenacoum (PT 14, also PPP). However none of these compounds could be detected at concentrations above the LOQ of 5 ng/g dry weight for bifenthrin or above a LOQ of 2 ng/g for the other compounds.

In some programmes samples are stored (specimen banks), but up to now no study on relevant rodenticides was performed. Here cooperation with institutions operating the programmes may be promising. An investigation of time series of appropriate samples from the archives would allow a retrospective analysis over several years. By this approach the consequences of recent changes of the authorisation (as PPP or biocide) of relevant rodenticides in recent years could be assessed.

Table 6 presents a proposal for a biocide monitoring in raptors. The approach is based on the scenario that rodenticides are taken up by rodents from baits and that these later on become prey of raptors. Information sources for biocide monitoring data for raptors are given in Table 7. A list of compounds which are applied as rodenticides is shown in Table 8. All substances are on the BPR list of approved substances for PA 14. Currently only difenacoum is also authorised as PPP.

Table 6: Overview of the biocide monitoring proposal for raptors. It is assumed that rodenticides are taken up by rodents from baits and that these become prey of raptors. Monitoring approach: survey.

Criterion	Specification	Comment
Matrix	Raptors	Raptor tissue (e.g., liver) or eggs
Relevant PTs and typical substances	PT 14 (rodenticides)	see Table 8; examples for detected PT 14 compounds: brodifacoum, bromadiolone, difenacoum and flocoumafen
Monitoring approach	Survey: opportunistic biota monitoring	Sampling of raptors found dead
Scale of monitoring	Depends on availability of samples; currently samples are primarily available for the Eastern part of Germany	Retrospective monitoring possible since appropriate samples are available in specimen banks
Relevant sites	Selection criteria: nearby potential biocide applications in near-natural environments	e.g., near farm buildings or in suburban areas
Relevant monitoring programmes in Germany/Europe	1) Peregrine falcon egg monitoring (LUBW Karlsruhe; von der Trenck 2012) 2) Raptor specimen bank of	In some programmes only samples are stored (specimen bank), but up to now no study on relevant rodenticides was

Criterion	Specification	Comment
	dead found organisms (IZW Berlin) 3) Programmes in UK, Norway, Denmark (see Workshop report, Jäger et al. 2013) 4) EURAPMON network (www.eurapmon.net); see overview of existing raptor contaminant monitoring activities in Europe in Gómez-Ramírez et al. 2014	performed Ad 2) the samples from IZW Berlin may be used in a co-operation project (e.g., funding of a Ph.D. thesis); contact: Dr. Oliver Krone, Leibniz Institute for Zoo and Wildlife Research, Berlin Ad 4) contact: e.g., via Prof. Richard Shore, UK Centre for Ecology and Hydrology, Lancaster Environment Centre, Lancaster, UK (member of the EURAPMON steering committee)
Appropriate analytical methods	Available, e.g. Christensen et al. (2012), Hughes et al. (2013), Langford et al. 2013, Tosh et al. (2012)	Studies applied multi-methods covering most of the relevant rodenticides
Limits of detection (LOD) / Limits of quantification (LOQ)	Walker et al. (2008): LODs were 0.045, 0.013, 0.002 and 0.050 µg/g wet weight for bromadiolone, difenacoum, flocoumafen and brodifacoum, respectively	1 g of tissue was applied; for quantification an HPLC method with fluorescence detection was used
Availability of labelled standard compounds	Not yet available	Example for alternative approaches: Langford et al. (2013) used coumachlor as an internal standard; Walker et al. (2012) applied external standard calibrations for the target compounds

Table 7: Examples for available biocide data from the monitoring of raptors.

Type of information	Description	Comment/Source
(Online) data sources	UK Predatory Bird Monitoring Scheme	Annual reports available (https://wiki.ceh.ac.uk/display/pbms/Home)
Literature	Several reports were published; examples for compounds detected in raptor tissue: brodifacoum, bromadiolone, difenacoum and flocoumafen	Walker et al. (2008), Christensen et al. (2012), Walker et al. (2012), Hughes et al. (2013), Langford et al. (2013)

Table 8: Biocides relevant for monitoring in raptors (approved substances for PT 14, rodenticides).

Substance	CAS No.	Biocide product type	PPP authorisation (in Germany)
Brodifacoum§	56073-10-0	14	until 2010
Bromadiolone§	28772-56-7	14	until 2011
Chloralose (Alphachloralose)$	15879-93-3	14	until 1976
Chlorophacinone#	3691-35-8	14	until 2010
Coumatetralyl#	5836-29-3	14	until 2004
Difenacoum§	56073-07-5	14	yes
Difethialone§	104653-34-1	14	until 2004
Flocoumafen§	90035-08-8	14	until 2003
Warfarin#	81-81-2	14	until 2012
Warfarin sodium#	129-06-6	14	until 1974

# first generation anticoagulant rodenticides. § second generation anticoagulant rodenticides.
$ also used as an anaesthetic and sedative in neuroscience and veterinary medicine.

The result from the prioritisation approach (Rüdel and Fliedner 2014) for biota in the terrestrial environment is shown in Table 9 (only PT 14 compounds selected). On basis of the EU biocide Assessment Reports the listed compounds are considered as persistent (or potentially persistent in case of brodifacoum) and as relevant for secondary poisoning of predators.

Table 9: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): rodenticides relevant for monitoring in terrestrial biota. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of terrestrial monitoring, BCF (fish) › 2000, not “readily biodegradable”, all rodenticides.

Ranking TERRESTRIAL BIOTA	CAS no.	PPP status (in Germany)	PT(s)	BCF (fish)$	Persistence	SCORE #
Compound		Authorised until			(as score)§	Terrestrial monitoring
Flocoumafen	90035-08-8	2003	14	36134	5	30
Difethialone	104653-34-1	2004	14	40000	5	30
Brodifacoum	56073-10-0	2010	14	35134	4	27
Difenacoum	56073-07-5	›2013	14	35645	4	27

PPP - plant protection product. § score from 0 = readily biodegradable to 5 = very persistent. # score for the relevance for monitoring the listed compounds in the terrestrial environment based on the criteria described in Rüdel and Fliedner (2014). $ BCF for fish was chosen since BCF for terrestrial organisms were not available for most compounds in the data set based on the EU biocide Assessment Reports.

4.3 Monitoring of the aquatic environment

4.3.1 Water phase

The water phase monitoring is well established in most countries. In Germany it is performed in compliance to the Water Framework Directive (WFD; 2000/60/EC, EC 2000) and daughter directives (2008/105/EC, EC 2008 and 2013/39/EU, EU 2013) and the German surface water ordinance (Oberflächengewässerverordnung; OGewV 2011). For the WFD surface water monitoring a guidance document is available (Guidance on surface chemical water monitoring under the Water Framework Directive; EC 2009b).

The WFD applies different monitoring strategies (2000/60/EC, EC 2000; Guidance on surface water chemical monitoring under the WFD, EC 2009b). The monitoring approaches are further specified in the German surface water ordinance (OGewV 2011).

Surveillance monitoring is applied to provide information to supplement and validate the water body impact assessment, to support the efficient and effective design of future monitoring programmes, and to allow the assessment of long-term changes in natural conditions and long-term changes resulting from anthropogenic activities. Sampling points should include major water bodies (rivers, lakes) as well as points at the downstream end of relevant sub-catchments. It is recommended to install fixed monitoring stations and automatic samplers allowing the collection of mixed samples (EC 2009b). For priority substances a monthly sampling of water bodies is applied while for river basin-specific substances the sampling frequency is 4 - 13 per year (at least once every six years for surveillance monitoring; OGewV 2011). For priority substances in biota a semi-annually or annually sampling is applied (at least once every three years; OGewV 2011).

An operational monitoring should be applied to establish the status of water bodies identified as being at risk of failing to meet environmental objectives, and to assess changes in the status of those water bodies resulting from possibly applied mitigation measures. Contrary to surveillance monitoring, operational monitoring is a spatially and temporally flexible monitoring approach (EC 2009b). If local sources can be excluded, a low number of water samples from several representative water bodies is regarded as sufficient to identify non-problem areas affected only by diffuse input (e.g., by long-range transport). The monitoring is intended to cover all priority substances as well as other pollutants discharged in significant amounts to the respective water body. For priority substances a monthly sampling of water bodies is applied while for river basin-specific substances the sampling frequency is 4 - 13 per year (at least once every three years for operational monitoring; OGewV 2011).

An investigative monitoring may be applied if reasons for exceedances of environmental objectives in a water body are unknown, or the surveillance monitoring indicated that the environmental objectives may not be achieved. Investigative monitoring may also applied to ensure that water bodies used for drinking water abstraction are not endangered by accidental pollution (EC 2009b).

A trend monitoring is considered for compounds which tend to accumulate in biota, suspended particulate matter or sediments (e.g., hydrophobic/lipophilic substances). For those compounds the long-term trend has to be determined in a relevant matrix (sampling every three years; OGewV 2011).

The WFD surface water monitoring is in the responsibility of the German federal states. A map with monitoring sites in one of the German federal states is shown in Figure 2.

Several biocides are already covered by the WFD surface water monitoring or in Germany as national relevant pollutants by the OGewV (2011) (Table 10). Monitoring data are provided by the responsible federal states either in online databases via the internet or in reports (mostly also available online).

Moreover, aggregated monitoring data for the covered substances for Germany are available since the data are compiled in a databank at the Umweltbundesamt (for EU reporting obligations). These data may be used also for the purpose of a biocide monitoring as proposed in this project.

Figure 2: Measurement sites in the German federal state of North Rhine Westphalia. Red dots - sites in the Rhine river, blue dots - sites in tributaries.

Table 10: Biocides included in the EU biocides review programme covered by surface water monitoring according to WFD (2000/60/EC, EC 2000) and daughter directives (2008/105/EC, EC 2008 and 2013/39/EU, EU 2013) or a German national regulation (German Surface Water Ordinance, OGewV 2011).
AA - annual average, EQS - environmental quality standard; MAC - maximum allowable concentration; PT - biocides product type.

Biocide name	CAS no.	PT	Monitoring obligation	Comment
Cybutryne	28159-98-0	21	2013/39/EU	AA and MAC EQS water; to be monitored by Dec. 2018
Cypermethrin	52315-07-8	8, 18	2013/39/EU	AA and MAC EQS water; to be monitored by Dec. 2018
Dichlorvos	62-73-7	Non-inclusion decision	2013/39/EU; OGewV 2011	AA and MAC EQS water; to be monitored by Dec. 2018
Diuron	330-54-1	7, 10	2008/105/EC; 2013/39/EU	AA and MAC EQS water
Isoproturon	34123-59-6	7, 10	2008/105/EC; 2013/39/EU	AA and MAC EQS water
Naphthalene	91-20-3	Non-inclusion decision	2008/105/EC; 2013/39/EU	AA and MAC EQS water; 2013/39/EU states lower EQS as compared to 2008/105/EC
Terbutryn	886-50-0	7, 9, 10	2013/39/EU	AA and MAC EQS water; to be monitored by Dec. 2018
Chlorotoluron	15545-48-9	Non-inclusion decision	OGewV 2011	AA EQS water
Diazinon	333-41-5	Non-inclusion decision	OGewV 2011	AA EQS water
Fenitrothion	122-14-5	Non-inclusion decision	OGewV 2011	AA EQS water
Monolinuron	1746-81-2	2	OGewV 2011	AA EQS water
Prometryn	7287-19-6	Non-inclusion decision	OGewV 2011	AA EQS water
Propiconazole	60207-90-1	7, 8, 9	OGewV 2011	AA EQS water
Terbuthylazine	5915-41-3	Non-inclusion decision	OGewV 2011	AA EQS water

For a biocide monitoring primarily limnic waters seem to be relevant. A monitoring of marine and coastal waters has lower priority for most biocides because concentrations in marine waters can be expected to be lower than in limnic waters. Thus a broader monitoring for marine waters should be discussed after more occurrence data on biocides in limnic waters are available.

Exceptions are monitoring studies on antifouling (PT 21) compounds. These seem more relevant in the marine environment due to traffic of large marine vessels and docking activities in open sea harbors (marine/estuarine sites). Thus especially investigations in harbors (and marinas for leisure boats) could help to follow environmental burdens by antifouling biocides and possible changes by phasing-out of compounds (see section 4.3.2).

For the formerly used organotin antifoulings (TBT, tributyltin compounds) the decrease of burdens could be documented in several studies. Due to analytical restrictions monitoring is conducted mainly in sediment and biota samples (e.g., in liver of harbour porpoises from UK waters, Law et al. 2012; for Germany, e.g., in North Sea and Baltic Sea biota in studies with archived samples from the German Environmental Specimen Bank; Rüdel et al. 2009). Furdek et al. (2012) report TBT water data for 48 locations at the Croatian Adriatic Coast from 2009/2010. TBT and degradation products (expressed on base of the tin content) ranged from about 0.5 to 28 ng/L Sn in seawater. At Cuxhaven (Elbe estuary) TBT levels were below the LOQ of 4 ng/L TBT or < 3 ng/L Sn (FGG Elbe data portal; www.fgg-elbe.de/elbe-datenportal-en.html).

An overview of the proposed implementation of a biocides monitoring of limnic surface waters in Germany is presented in Table 11, while examples of information sources for surface water monitoring programmes are given in Table 12. The whole water phase should be used as sample (in compliance with the requirements of WFD monitoring of organic substances, EU 2013; see also Guidance on surface chemical water monitoring under the Water Framework Directive, EC 2009b).

For surface water monitoring it should be considered to normalise the determined concentration data to the mean annual flow. Alternatively the mass flow from different years may be compared. Both approaches avoid a bias from different flow situations on concentrations measured at different sampling events (e.g., dilution during flood events).

The monitoring should be on a national scale and cover those sites which are also used for the WFD compliance monitoring (so called “LAWA Übersichtsmessstellen”). Monitoring data for these sites are reported annually to the UBA so that a retrospective data analysis is possible. An example of a time series from surface water monitoring of triclosan is shown in Figure 3.

In some cases it may be appropriate to perform a screening study with only a limited number of sites. For this approach collaboration with authorities of the German federal states may be constructive (to include the substances, e.g., into a WFD surveillance monitoring). For biocides used in urban areas the monitoring programmes in the states of Berlin, Hamburg or North Rhine Westphalia (Ruhr conurbation) are especially relevant. If the screening confirms the relevance of a compound in the aquatic environment, the compound may be recommended for the national monitoring programme (ideally by identification as river basin-specific substance; in this case also an environmental quality standard has to be derived).

In order to assess whether sewage and/or effluents of sewage treatment plants could be the possible source of findings of biocides in surface waters, appropriate tracer compounds may be analysed parallel to the target compounds (e.g., acesulfam; Buerge and Poiger 2011).

In Table 13 the currently authorised biocides with relevance for surface water are compiled. According to the criteria emission and effects relevance of the prioritisation proposal (report for work package III, Rüdel and Fliedner 2014) DCOIT, triclosan, BIT and IPBC are scored highest.

Figure 3: Time series of triclosan concentrations in weekly water samples from the Elbe river, site Zehren, period 2007 - 2012 (data are µg/L triclosan, data below the LOQ of 0.005 µg/L are reported as concentration equal to 50% of the LOQ = 0.0025 µg/L). By LAWA an EQS of 0.02 µg/L as annual average was proposed.

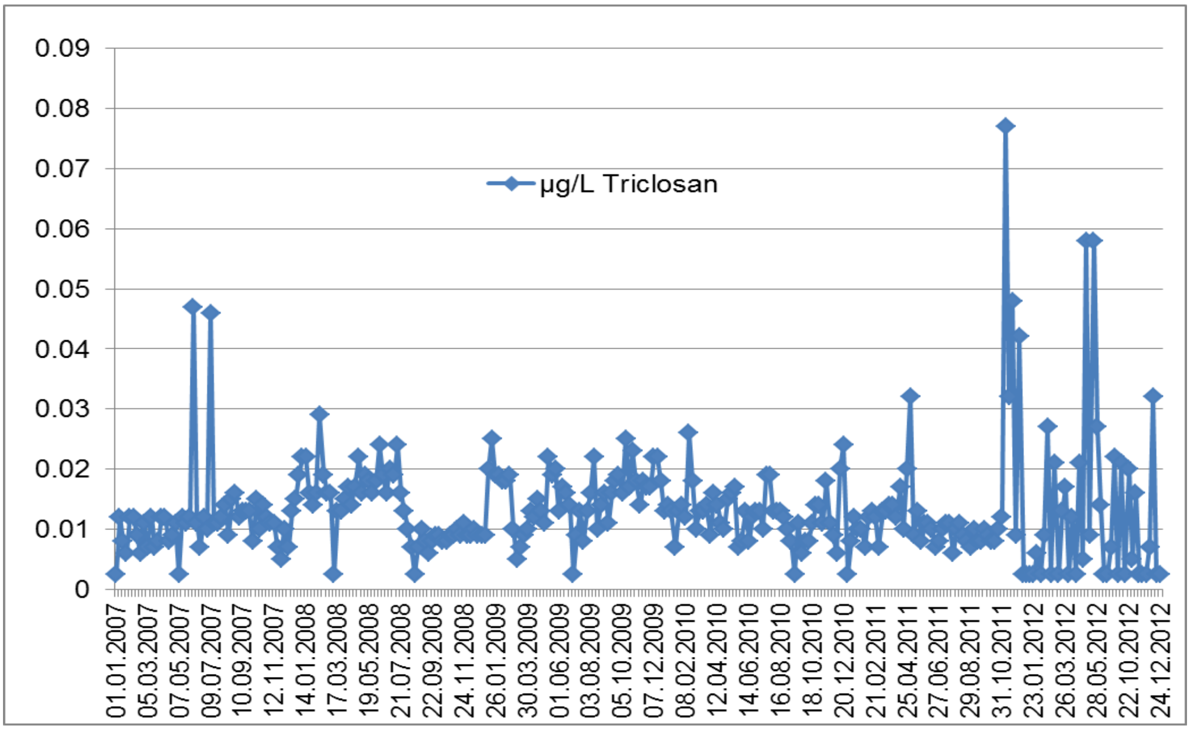


Table 11: Overview of the biocide monitoring proposal for surface waters (water phase). Monitoring approach: routine monitoring.

Criterion	Specification	Comment
Matrix	Water phase	According to WFD requirements whole water phase for organic compounds (i.e. unfiltered; EU 2013: total concentrations in the whole water sample including suspended solids)
Relevant PTs and typical substances	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 from direct inputs; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via STPs	Examples for detected compounds: Triclocarban (non-inclusion decision for BPD/BPR list of approved substances), triclosan (PT 1, 2, 7, 9) and TP methyltriclosan, cybutryne (Irgarol; PT 21, until 2011 also authorised for PT 7, 9, 10), diuron (PT 7, 10); refer to Table 13 for prioritised compounds
Monitoring approach	Routine monitoring of water bodies: e.g., monthly sampling of the water phase (WFD surveillance monitoring) To identify biocide relevant emissions it may be appropriate to limit	Ideally pooled samples (e.g., weekly) are taken and combined to a monthly sample; this approach allows detecting substances with intermittent emission characteristics By this approach the number of samplings may be reduced; however, for a

Criterion	Specification	Comment
	the sampling in certain cases to specific sites (e.g., urban sites, main usage as biocide expected for compound also authorised as PPP) or to certain time periods (e.g., winter, no PPP applications expected)	thorough interpretation of the differentiation of monitoring findings between PPP/biocide usage also data from other seasons and other sites may be helpful
Scale of monitoring	National scale	Some biocides are already covered by monitoring obligations by WFD (as amended in EU 2013) or in Germany by OGewV (2011): e.g., isoproturon, diuron, propiconazole (see Table 10)
Relevant sites	Due to the varying emission patterns of the different PTs all kind of water bodies seem relevant	To monitor indirect inputs, sites in larger rivers which are influenced by effluents of STPs seem most relevant (for comparison also samplings upstream of the respective STPs should be included) Measurements in smaller water bodies may be relevant if specific exposed, e.g., potential exposure to biocides leached in (new) settlements from façades which are transported via stormwater to water bodies
Relevant monitoring programmes in Germany/Europe	WFD compliance monitoring (in Germany performed by federal states)	Data from ca. 260 LAWA monitoring sites are reported to the UBA (section Inland surface waters, II 2.4); biocides data may be retrieved by a databank search (a proposal of relevant compounds was provided with the status report for the current project in May 2013)
Appropriate sampling methods	Guidance on surface water chemical monitoring (EC 2009b); guidance on the design of sampling programmes and sampling techniques (ISO 5667-1 2006), guidance on sampling of surface waters (DIN 38402-15 2010), guidance on sample preservation (ISO 5667-3 2012)	Procedures according to WFD requirements, application of national or international standards
Appropriate analytical methods	GC-MS or HPLC-MS methods according to substance properties; see, e.g., Wick et al. (2010) for a HPLC-MS multi-method for biocides	Requirements for methods and laboratories are described in OGewV (2011)

Criterion	Specification	Comment
Limits of detection (LOD) / Limits of quantification (LOQ)	Largely varying depending on compound and applied analytical method	LOQ should be lower than PNEC (e.g., 30% of the PNEC)
Availability of labelled standard compounds	e.g., standards from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; in Germany available via LGC Standards GmbH, Wesel): triclosan ($^{13}C_{12}$, 99%), methyltriclosan (ring-$^{13}C_{12}$, 99%), triclocarban (4'-chlorophenyl-$^{13}C_6$, 99%) e.g. PESTANAL standards from Sigma-Aldrich: isoproturon-D6; e.g. standards from Dr. Ehrenstorfer: imazalil-D5 (2-propenyl-D5), propiconazole-D5 (2,2,3,3,3-propyl-D5), tebuconazole-D6 (ethylene-D4, methylene-D2) e.g., standards from Toronto Research Chemicals, in Germany available via BIOZOL Diagnostica Vertrieb GmbH, Eching: Irgarol-D9	Especially for biocides which are also used as PPP labelled standards are available

Table 12: Examples for available biocide data from the monitoring of surface waters (water phase).

Type of information	Description	Comment/Source
(Online) data sources	Some German federal states publish surface water monitoring data via the internet (e.g., North Rhine Westphalia.	Example: http://luadb.lds.nrw.de/LUA/hygon/pegel.php?messstellen_nr=000504&guete=tabelle, folder "Gewässergüte"; only a few relevant biocides are covered; partly only current data are available (no aggregated data from earlier measurements)
	Aggregated data from several federal states for the Elbe are available by FGG Elbe	Source: www.fgg-elbe.de/elbe-datenportal-en.html, select "Start - Data Information System Elbe" (German Version only)
	Internet portal of the NORMAN network: the EMPODAT database contains data on, e.g., the biocides triclosan, DEET, carbendazim, cybutryne (Irgarol), imidacloprid	Source: www.norman-network.com/empodat/
	The Netherlands operate also a database on pesticide monitoring data in surface waters	Source: http://www.bestrijdingsmiddelenatlas.nl/atlas.aspx

Type of information	Description	Comment/Source
Literature	Assessments, e.g., for chlorotoluron, diuron, isoproturon, terbuthylazine and no-longer authorised biocides like lindane and TBT	Report for Germany: Wasserwirtschaft in Deutschland, Teil Gewässergüte (Arle et al. 2010, 2013)
	Data on triclosan from occurrences at 802 monitoring sites in the Elbe River basin	Von der Ohe et al. (2012)
	Data on WFD relevant biocides in limnic and coastal waters from Denmark	Vorkamp et al. (2014)

Table 13: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for monitoring in the water phase of surface waters. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of monitoring in water, K_{OC} < 100000, not “readily biodegradable” (or no data on degradability), TOP 10 compounds with relevant PT(s) and without current PPP authorisation.

Ranking WATER Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	Persistence (as score)§	SCORE Monitoring in water#
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	-	7, 8, 9, 10, 11, 21	2	378
Triclosan	3380-34-5	-	1,2,7,9	5	280
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	-	2, 6, 9, 11, 12, 13	3	280
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	-	6, 7, 8, 9, 10, 12, 13	2	240
Methyltriclosan (Triclosan TP)	4640-01-1	-	1,2,7,9	5	224
Dichlofluanid	1085-98-9	2003	7, 8, 21	3	192
Tolylfluanid	731-27-1	2010	7, 8, 21	2	168
(DCOIT-TP) 2-chloro-2-(n-octylcarbamoyl)-1-ethene sulfonic acid	-	-	7, 8, 9, 10, 11, 21	3	168

Ranking WATER Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	Persistence (as score)§	SCORE Monitoring in water#
NNOOA (DCOIT-TP EW) N-(n-octyl) oxam-ic acid	-	-	7, 8, 9, 10, 11, 21	2	168
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	3	162

PPP - plant protection product. § score from 0 = readily biodegradable to 5 = very persistent. # score for the relevance for monitoring the listed compounds in the aquatic environment based on the criteria described in Rüdel and Fliedner (2014).

4.3.2 Monitoring of antifoulings in the water phase

Currently UBA has commissioned a project to assess the reliability of antifouling exposure estimations (as described in Emission Scenario Documents, ESDs) in the context of the EU biocidal registration procedure ("Leisure boat inventory and antifouling biocides in German surface waters", FKZ 3711 67 432; presentation and poster of Watermann and Feibicke at the Biocides Monitoring Workshop, Berlin, November 2012; Jäger et al. 2013). The work focuses on the actual situation in German inland waters for the use phase of antifoulings in the area of marinas. Antifoulings are used, e.g., on boats for recreational use in coastal and inland waters. They are part of underwater coatings that prevent colonisation of animals, plants and microorganisms on boat hulls.

In the UBA project a nationwide inventory of marinas and their boats in German inland and coastal waters is carried out. First, the relevant structural data on marinas are statistically evaluated and local and regional pollution hotspots are identified. Thereafter, water levels of a group of antifoulings in marinas will be determined quantitatively. This measurement campaign is scheduled for one summer in the project period at sites with high boat densities. The selected sites should reflect the variety of biocide concentrations found in German leisure boat harbours. Furthermore, the selected marinas should cover both types of marinas, those that fit well into the routine exposure models and those that are substantially different from the standard scenario.

In Table 14 the monitoring approach for antifoulings at marinas in coastal and inland waters is characterised. The currently available monitoring data of antifoulings in coastal and inland waters are given in Table 15. Table 16 displays the antifouling biocides currently assessed in the EU biocides review programme according to the BPD (EC 1998).

As an example, time series data from a cybutryne surface water monitoring in the Rhine river and its tributary Neckar over a period of five years are shown in Figure 4.

Table 14: Overview of the biocide monitoring proposal for antifoulings at marinas in coastal and inland waters (water phase).
Monitoring approach: research project or screening.

Criterion	Specification	Comment
Matrix	Water phase	According to WFD requirements whole water phase for organic compounds (i.e. unfiltered; EU 2013: total concentrations in the whole water sample including suspended solids)
Relevant PTs and typical substances	PT 21	Examples for detected compounds: cybutryne (Irgarol; PT 21, until 2011 also authorised for PT 7, 9, 10), DCOIT (also authorised for PT 7, 8, 9, 10, 11); beside active ingredients also transformation products may be relevant (e.g., "metabolite M1" for cybutryne (Irgarol)
Monitoring approach	Research project or screening: grab water samples at marinas	Single samplings per site
Scale of monitoring	Marinas in coastal and inland waters	50 selected sites
Relevant sites	Sites should cover both types of marinas, those that fit well into the routine exposure models and those that are substantially different from the standard scenario	See results of current research project "Leisure boat inventory and antifouling biocides in German surface waters" (FKZ 3711 67 432)
Appropriate sampling methods	Refer to Table 11	WFD approach should be applied
Appropriate analytical methods	GC-MS or HPLC-MS methods according to substance properties; see, e.g.: Wick et al. (2010) for a HPLC-MS multi-method for biocides (e.g., cybutryne and DCOIT are covered); Giráldez et al. (2013) for a method based on stir bar sorptive extraction thermal desorption GC-MS (e.g., dichlofluanid, DCOIT and cybutryne are covered)	Requirements for methods and laboratories described in OGewV (2011); starting from 2018 AA EQS (2.5 ng/L) and MAC EQS (16 ng/L) in surface waters have to be complied to
Relevant monitoring programmes in Germany/Europe	May be part of the WFD operational monitoring of the German federal states	Data in marinas may be available also from some of the German federal states (e.g., Bavaria; contribution of Sengl et al. at the Biocides Monitoring Workshop,

Criterion	Specification	Comment
		Berlin, November 2012; Jäger et al. 2013)
Limits of detection (LOD) / Limits of quantification (LOQ)	Depending on compound and method	Cybutryne 0.5 ng/L, DCOIT 1 ng/L (Wick et al. 2010); cybutryne 10 ng/L, DCOIT 30 ng/L (Giráldez et al. 2013)
Availability of labelled standard compounds	e.g., Irgarol-D9 standard from Toronto Research Chemicals, in Germany available via BIOZOL Diagnostica Vertrieb GmbH, Eching	For cybutryne alternatively tebuconazole-D6 may be used as internal standard (preliminary results by J. Schwarzbauer et al., RWTH Aachen, from the method development for working package V of this project)

Table 15: Examples for available biocide data from the monitoring of antifoulings in coastal and inland waters.

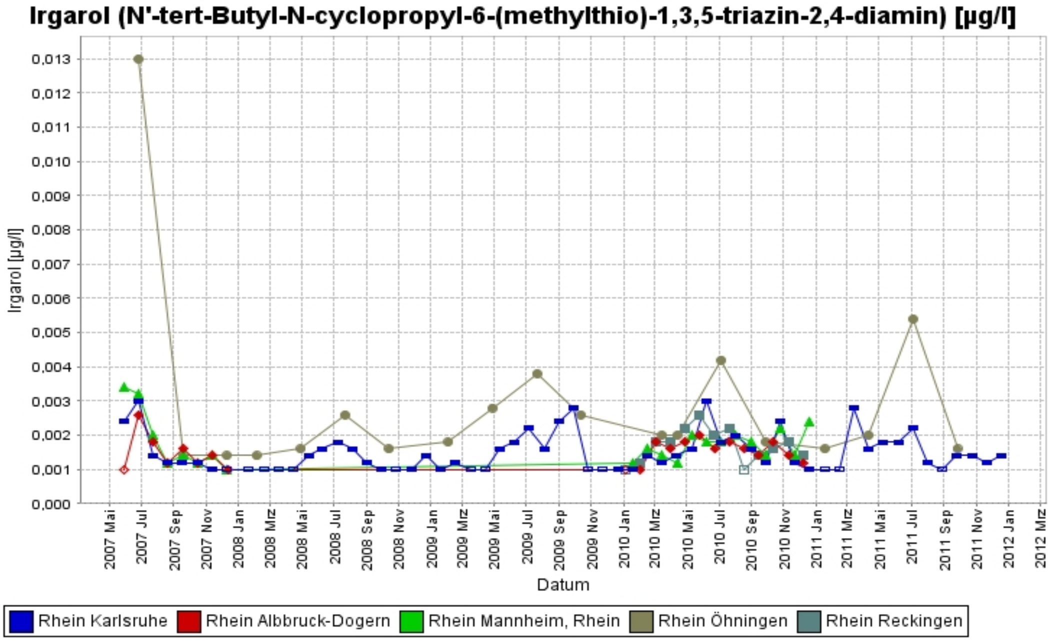
Type of information	Description	Comment/Source
(Online) data sources	Some German federal states publish surface water monitoring data via the internet; however, not all antifoulings are covered (mostly only those regulated by WFD or OGewV 2011)	Example: Baden-Württemberg http://jdkfg.lubw.baden-wuerttemberg.de/servlet/is/300/
	Aggregated data from several federal states for the Elbe are available by FGG Elbe	Source: www.fgg-elbe.de/elbe-datenportal-en.html, select "Start - Data Information System Elbe" (German Version only)
	Internet portal of the NORMAN network: the EMPODAT database contains currently data on cybutryne (Irgarol) and tolylfluanid	Source: www.norman-network.com/empodat/
Literature	Information on German monitoring data for cybutryne (Irgarol) and no-longer authorised biocides like TBT	Report for Germany: Wasserwirtschaft in Deutschland, Teil Gewässergüte (Arle et al. 2010, 2013)
	Data on cybutryne (Irgarol) in limnic and coastal waters from Denmark	Vorkamp et al. (2014)

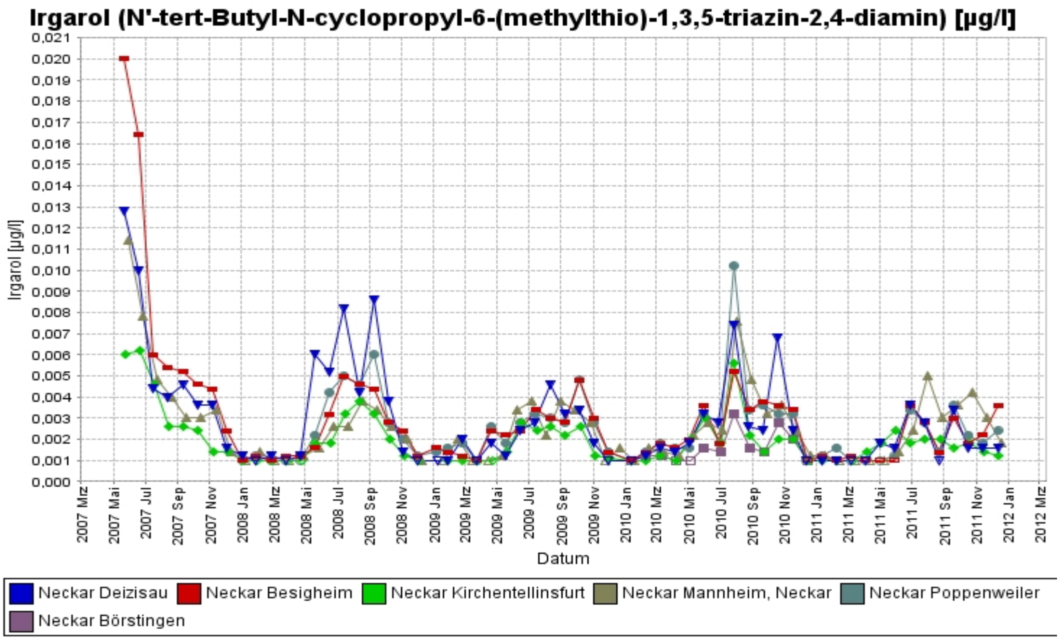
Table 16: List of biocides currently assessed in the EU biocides review programme as antifoulings (PT 21).

Ranking WATER Compound	CAS no.	PNEC§ [µg/L]	PT(s) in review program	Score Monitoring in water#
4,5-dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	0.034	7, 8, 9, 10, 11, 21	378
Dichlofluanid	1085-98-9	0.053	7, 8, 21 $	192
Tolylfluanid	731-27-1	0.265	7, 8, 21 &	168
Cybutryne (Irgarol)	28159-98-0	0.0058	21	40
Copper pyrithione	14915-37-8	0.0036	21	55
Zineb	12122-67-7	0.2244	21 ¥	25
Zinc pyrithione	13463-41-7	-	2, 6, 7, 9, 10, 21	-
Copper thiocyanate	1111-67-7	-	21	-
Dicopper oxide	1317-39-1	-	21	-
Copper	7440-50-8	-	21	-

§ PNEC taken from EU biocides Doc I Assessment Reports. # score for the relevance for monitoring the listed compounds in the aquatic environment based on the criteria described in Rüdel and Fliedner (2014). – no data/not assessed. $ PPP authorisation until 2003. & PPP authorisation until 2010. ¥ PPP authorisation until 1997.

Figure 4: Time series of cybutryne (Irgarol) concentrations in water samples from the upper Rhine river (top; five sites) and its tributary Neckar (bottom, six sites), period 2007 - 2011 (data are µg/L Cybutryne). Data source: LUBW (2014).





4.3.3 Suspended particulate matter (SPM) and sediments

Suspended particulate matter (SPM) and (surface) sediments may be investigated for biocides which tend to adsorb or bind to inorganic and organic particles and materials. SPM can be sampled as alternative to sediments (Schubert et al. 2012). It may be viewed as a surrogate of surface sediment (remobilised upstream surface sediment and/or material which is expected to be deposited downstream the sampling site). For a trend monitoring SPM samples seem to be more appropriate since SPM can be sampled more reproducibly. Surface sediment concentrations of target compounds may change from year to year due to flood events. However, a sampling of sediment cores offers the possibility of a retrospective monitoring (if the core is undisturbed the age of specific layers can be assessed by radiometrical methods). Table 17 gives an overview of the biocide monitoring proposal for suspended particulate matter (SPM) and sediments and Table 18 gives examples for information sources for the monitoring of biocides in suspended particulate matter (SPM) and sediments.

For the purpose of the here proposed biocides monitoring it seems more appropriate to apply passive sampling with sedimentation traps as compared to SPM sampling with a centrifuge. The sampling with traps allows a time integrative sampling over, e.g., a month while a centrifuge can be operated only up to a few days.

To realise a SPM monitoring in Germany it is suggested to use the potential of the German Environmental Specimen Bank (ESB; www.umweltprobenbank.de/en/). The programme covers a SPM sampling at 16 river sites since the years 2005/2006 (Figure 5). The archived samples can be used for a retrospective monitoring. Most sites are influenced by effluents from STPs (Table 19; based on data in Subedi et al. 2012). Sites shortly downstream of large STPs (< 15 km distance, > 100000 inhabitant equivalents per capita) are, e.g., Blankenese (E5 in Figure 5), Weil (R1) or Güdingen (S1).

In a previous investigation methyltriclosan traces were detected in selected SPM samples collected according to the German ESB protocols while triclosan levels were below the LOQ (Rüdel et al. 2013). Recently a study was conducted in which SPM time series from the German ESB archive were analysed for the biocides cybutryne (Irgarol), propiconazole and tebuconazole (study commissioned by Umweltbundesamt in 2013, project 28 221; Schulz 2013). Figure 6 shows the respective results for cybutryne at the Saar sampling site S2 (Rehlingen). This study may be regarded as a feasibility study for the implementation of a SPM monitoring for polar compounds.

In Table 20 the biocides which were prioritised for a biocides monitoring in SPM (or sediments) are listed (work package III outcome; Rüdel und Fliedner 2014).

Table 17: Overview of the biocide monitoring proposal for suspended particulate matter (SPM) and sediment.
Monitoring approach: screening or survey.

Criterion	Specification	Comment
Matrix	Suspended particulate matter (SPM) and sediment	According to WFD requirements some compounds may be monitored also in SPM or sediments; according to OGewV (2011) for some metals compliance monitoring in SPM/sediments is required; thus SPM samples may be available from certain programmes which could be used for a biocides monitoring
Relevant PTs and typical substances	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 from direct inputs; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via	Examples for detected compounds: organotin compounds (now banned antifouling compounds) are frequently detected in sediments; triclosan (PT 1, 2, 7, 9) and several QAC; refer to

Criterion	Specification	Comment
	STPs	Table 20 for prioritised compounds
Monitoring approach	Screening or survey: Monthly sampling with sedimentation traps (WFD surveillance monitoring, WFD trend monitoring) Grab sampling for sediment Sampling of sediment cores	Time-integrative sampling For surface sediment sampling Cores allow dating of the sediment burdens
Scale of monitoring	National scale, coverage of all water bodies (rivers and lakes)	Parallel to WFD monitoring water phase monitoring (see section 4.3.1)
Relevant sites	SPM monitoring in larger rivers, sediment sampling in lakes	Sites in urban regions and those influenced by STP effluents; smaller rivers may not contain sufficient SPM
Relevant monitoring programmes in Germany/ Europe	WFD compliance monitoring (in Germany performed by federal states) German Environmental Specimen Bank	Compounds as listed in OGewV (2011) Archived samples from the German Environmental Specimen Bank allow a retrospective monitoring (samples from monthly samplings are combined to prepare an annual pooled sample)
Appropriate sampling methods	A standard operating procedure for the sampling of SPM with traps is available from the German Environmental Specimen Bank (http://www.umweltprobenbank.de/upb_static/fck/download/SOP_Schwebstoffe.pdf; in German language) Guidance on chemical monitoring of sediment and biota (EC 2010)	SPM is also sampled from several of the German federal states (e.g., at the Elbe river) Procedure according to WFD requirements
Appropriate analytical methods	GC or HPLC methods according to substance properties; see, e.g., Wick et al. (2010) for a HPLC multi-method for biocides	Requirements for methods and laboratories described in OGewV (2011); according to OGewV sediment analyses have to be performed on a fraction sieved ‹ 63 um
Limits of detection (LOD) / Limits of quantification (LOQ)	LOD for triclosan and methyl-triclosan in SPM: 0.1 ng/g dry weight LOD for cybutryne (Irgarol), tebuconazole and propiconazole in SPM: 0.1 ng/g dry weight	Rüdel et al. (2013) Schulz (2013)

Criterion	Specification	Comment
Availability of labelled standard compounds	e.g., standards from CIL, Inc. (in Germany available via LGC Standards GmbH, Wesel): triclosan (13C12, 99%), methyltriclosan (ring-13C12, 99%), trans-permethrin (phenoxy-13C6, 99%); cis-permethrin (phenoxy-13C6, 99%)	Alternative: use of labelled compounds with similar chemical properties or external calibration

Table 18: Examples for available biocide data from the monitoring of suspended particulate matter (SPM) and sediments.

Type of information	Description	Comment/Source
(Online) data sources	Aggregated data from several federal states for the Elbe are available by FGG Elbe, e.g., data, for organotin compounds (banned antifouling compounds)	Source: www.fgg-elbe.de/elbe-datenportal-en.html, Start - Data Information System Elbe (German Version only)
	Internet portal of the NORMAN network: data for SPM and sediments are available (but currently only data for few relevant biocides)	Source: www.norman-network.com/empodat/
Literature	Detection of methyltriclosan in SPM from the German Environmental Specimen Bank	Rüdel et al. (2013)
	In most sediment samples from Norwegian lakes and rivers triclosan was quantified (e.g., in sediment from Drammens river 0.02 - 11 ng/g dry weight, with increasing levels downstream)	Fjeld et al. (2004)
	Time series investigation of cybutryne (Irgarol) and the azole fungicides tebuconazole and propiconazole in archived SPM samples of the German Environmental Specimen Bank	Schulz (2013)
	In Norway the Zineb transformation product ethylenethiourea was detected in SPM from two marinas	Langford et al. (2012)
	In Sweden sediments were investigated for zinc pyrithione (in all samples below the detection limit) and cybutryne/Irgarol (quantified in 70% of the sediment samples at 2.5 - 20 ng/g dry weight)	Woldegiorgis et al. (2007)
	A study in Austria detected QAC in sediments: C12-benzalkonium chloride and C18-dialkyldimethylammonium chloride with maximum concentration of 3.6 µg/g and 2.1 µg/g	Martínez-Carballo et al. (2007b)

Figure 5: River sampling sites of the German Environmental Specimen Bank (ESB). Danube: D1 - Ulm, D2 - Kelheim, D3 - Jochenstein; Elbe: E1 - Prossen, E2 - Zehren, E3 - Barby, E4 - Cumlosen, E5 - Blankenese; Saale: Sa - Wettin; Mulde: Mu - Dessau; Rhine: R1 - Weil, R2 - Iffezheim, R3 - Koblenz, R4 - Bimmen; Saar: S1 - Güdingen, S2 - Rehlingen (B: Lake Belau, limnic reference site of the German ESB). Source: German Environmental Specimen Bank, Umweltbundesamt.

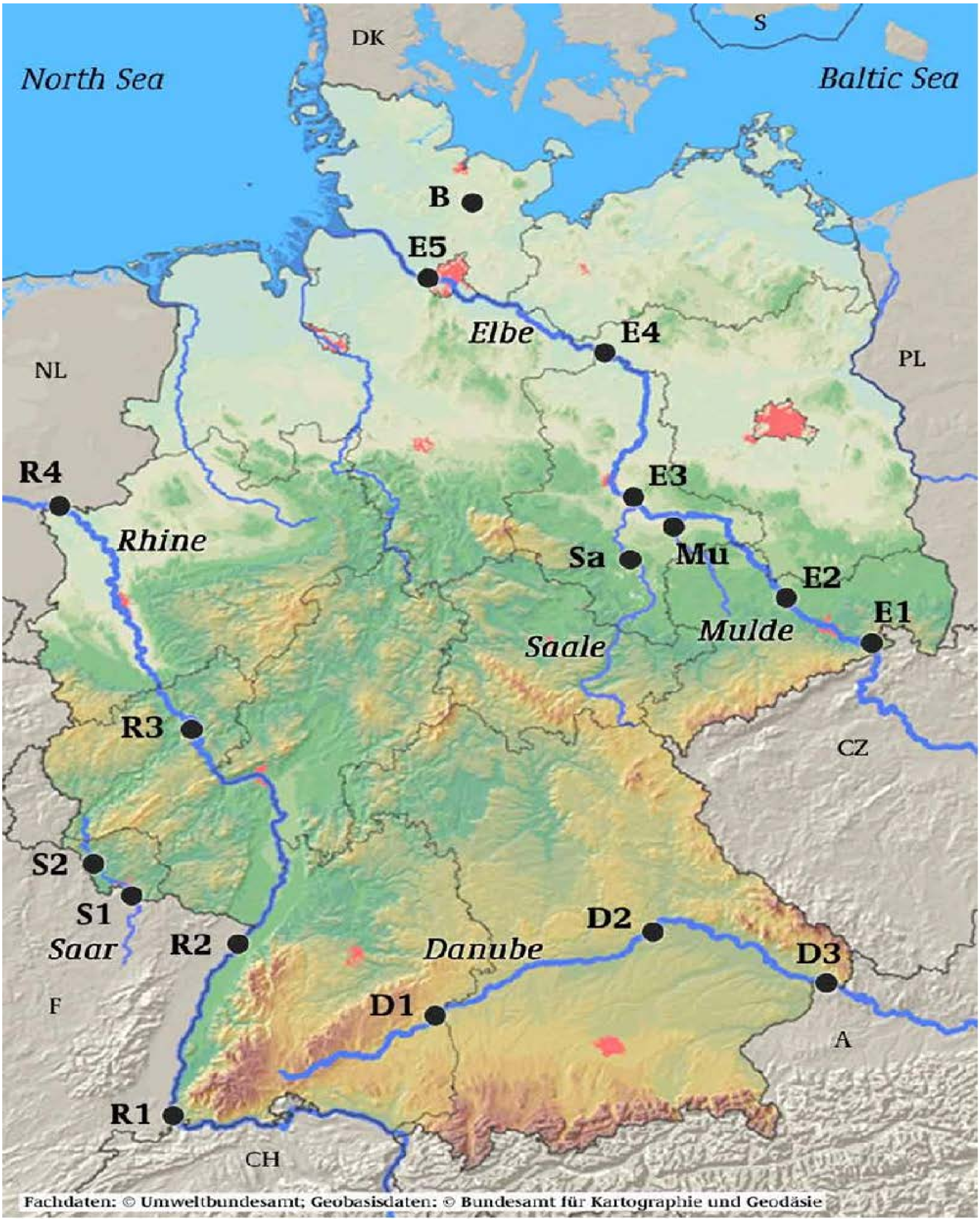


Table 19: STPs nearby or upstream of German ESB sampling locations. The shaded sites are influenced heavily by STPs (STP emissions of › 100000 inhabitant equivalents in the 15 km upstream stretch; no information for the sites Rhine/Koblenz, Elbe/Zehren and Elbe/Cumlosen; based on Subedi et al. 2012).

ESB sampling locations	MAF [m³ / s]	STPs	PSL [km]	IE [capita]	STPs capacity [m³ / d]
		Saar			
Güdingen (S1)	60	Brebach	0	135 000	up to 41 000
		Saargemünd	10.8	61 500	-
Rehlingen (S2)	80	Saarlouis	6.2	93 000	up to 48 000
		Ensdorf	13.7	58 000	up to 58 000
		Völklingen	19.7	80 000	up to 40 000
		Burbach	28.5	200 000	up to 60 000
		Rhine			
Weil (R1)	500	Basel	4.4	1 200 000	up to 120 000
		Chemie Basel	4.4	*	up to 9 500
		Steith	4.6	**	up to 4 200
Iffezheim (R2)	-	Rheinmünster	8.5	6 400	-
		Lichtenau	15.5	-	-
		Straßbourg	34.1	1 000 000	up to 240 000
		Kehl	35.4	48 000	about 8 000
		Offenburg	50.7	200 000	about 28 000
Bimmen (R4)	2000	Salmorth	6.9	40 833	up to 76 800
		Emmerich	14	126 736	up to 67 200
		Kalkar-Hönnepel	23.2	38 401	up to 27 744
		Xanten-Vynen	33.8	606	up to 2 400
		Xanten-Lüttingen	41.1	5 753	up to 17 280
		Wesel	50.1	19 900	up to 60 000
		Danube			
Ulm (D1)	100	Erbach	6.1	class 4	-
		Ehingen	22.3	class 4	-
		Rottenacker	26.8	class 4	-
		Donau-eschingen	181	148 000	up to 86 400
Kelheim (D2)	400	Saal	6.9	class 4	-
		Staubing	18.6	class 2	-

ESB sampling locations	MAF [m³ / s]	STPs	PSL [km]	IE [capita]	STPs capacity [m³ / d]
		Neustadt	29.4	class 4	-
		Ingolstadt	50.3	275 000	up to 156 000
Jochenstein (D3)	1000	Obernzell	0	class 3	-
		Thyrnau	5.6	class 3	-
		Achleiten	8	class 4	-
Elbe and tributaries					
Prossen (E1)	no data available, the sampling site is located at the Czech border; 23.5 km downstream the city of Decin (50 000 inhabitants), 48 km downstream the city of Usti and Labem (100 000 inhabitants)				
Barby (E3)	-	Aken	15.6	27 000	about 8 100
		Calbe	17.7	-	-
		Dessau	28.3	-	about 18 000
		Bernburg	34.2	-	-
		Coswig	50.4	20 000	-
		Wittenberg	68.9	-	-
		Halle-Nord	86.8	300 000	about 75 000
Blankenese (E5)	800	Köhlbrandhöft/ Dradenau	4	2 900 000	up to 1 641 600
		Geesthacht Düneberg	42.6	60 000	up to 5 800
Wettin, Saale river (SA)	115	Halle-Nord	15	300 000	about 75 000
		Leipzig-Rosental	63.7	628 000	-
Dessau, Mulde river (MU)	64	Bitterfeld-Wolfen	37.2	422 000	-

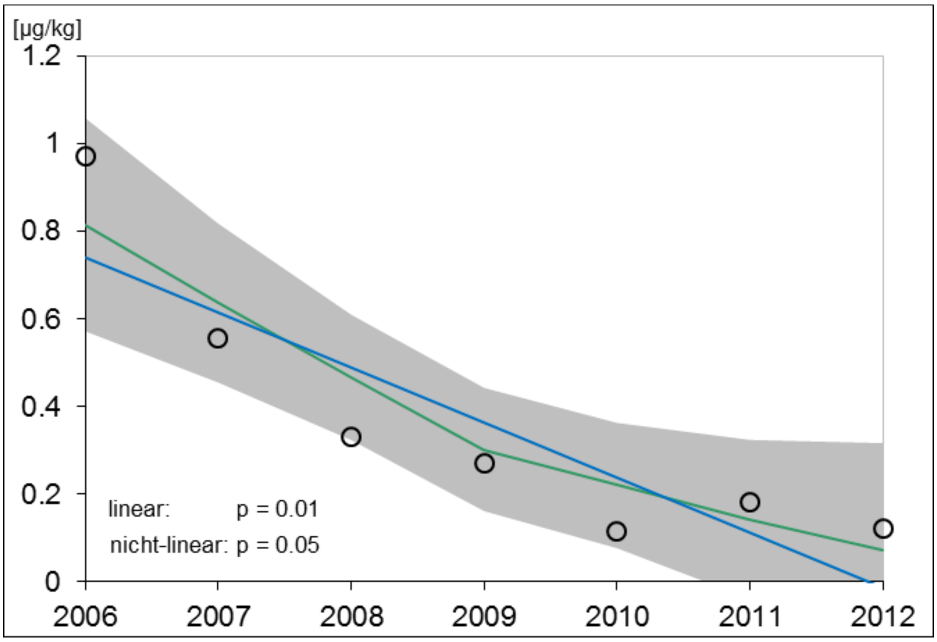
STP - sewage treatment plant. MAF - mean annual flow; PSL - proximity to the sampling locations. IE - inhabitant equivalents in capita. * STP of chemical industry: F. Hoffmann-LaRoche AG , Novartis Pharma AG, Ciba Chemie AG and Syngenta AG, right-hand side of the River Rhine. ** STP of chemical industry: Clariant, Ciba AG (Huningue) and Novartis Pharma AG (St. Johann), left-hand side of the River Rhine. Class 1: < 1000, class 2 = 1000 - 5000, class 3: 5000 - 10000, class 4: 10000 - 100000, class 5: > 100000.

Table 20: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for monitoring in suspended particulate matter (SPM) and sediments from surface waters. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of monitoring in water, K_{OC} › 10000, not "readily biodegradable" (or no information on degradability), TOP 10 compounds with relevant PT(s) and without current PPP authorisation.

Ranking SEDIMENT/SPM Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	K_{OC}	Persistence (as score) §	SCORE # Monitoring in water
Didecyldimethylammonium chloride (DDAC)	7173-51-5	-	1, 2, 3, 4, 6, 8, 10, 11, 12	1018685	1	240
Didecylmethyl-poly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	-	2, 4, 8, 9, 10, 11, 12	1103802	4	180
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	76900	3	162
Chlorfenapyr	122453-73-0	-	8, 18	11960	3	81
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	-	18	35171	2	48
Transfluthrin	118712-89-3	-	18	53703	3	48
(AEM 5772 TP) 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride	199111-50-7	-	2, 7, 9	6370000	2	45
Flufenoxuron	101463-69-8	-	8	157643	5	44
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	Keine	18	125893	5	42
Creosote	8001-58-9	Keine	8	14791	4	40

PPP - plant protection product. K_{OC} - soil organic carbon-water partitioning coefficient (from EU biocide Assessment Reports). § score from 0 = readily biodegradable to 5 = very persistent. # score for the relevance for monitoring the listed compounds in the aquatic environment based on the criteria described Rüdel and Fliedner (2014).

Figure 6: Time series for cybutryne (Irgarol) in suspended particulate matter (SPM) from the sampling site Saar/Rehlingen of the German Environmental Specimen Bank (ESB), period 2006 - 2012. Data are in µg/kg dry weight. Trend evaluation with the LOESS tool 1.0 (UBA 2013); the blue line is the smoothed linear trend line (significant at p = 0.01) and the shaded area marks the 95% confidence band.



Data source: Schulz 2013.

4.3.4 Aquatic biota

Aquatic biota (e.g., fish or mussels) may be investigated for biocides which tend to bioconcentrate or bioaccumulate. For a trend monitoring of lipophilic substances in limnic waters fish samples seem to be most appropriate (as long as no information is available that compounds are rapidly metabolised in fish tissues). In marine and limnic monitoring experience from both, fish and mussel sampling and analysis is available.

Limnic fish monitoring programmes are conducted in several countries (in Europe, e.g., in Sweden, UK and Germany). Fish monitoring is also considered for the WFD compliance monitoring for three compounds (according to the EQS directive, EC 2008: mercury, hexachlorobenzene and hexachloro-butadiene; further compounds have to be covered after implementation of the revised EQS directive 2013/39/EU, EU 2013). However, EU member states may decide to use alternative monitoring approaches for these compounds. In Germany some federal states are running fish (and partly mussel) monitoring programmes for limnic waters. Most programmes rely on an annual sampling according to standardised protocols. In most programmes liver and/or fillet are used for the investigations (since in the WFD EQS Directive the tissue for the biota investigations is not specified it is assumed that the whole fish is applied for analysis, at least if the EQS derives from the protection against secondary poisoning; however, whole fish preparation is currently only applied for small fish).

Table 21 gives an overview of the biocide monitoring proposal for aquatic biota in freshwater and Table 22 summarises information sources for monitoring programmes using limnic aquatic biota. To realise an aquatic biota monitoring in Germany it is suggested to use the potential of the German Environmental Specimen Bank (ESB; www.umweltprobenbank.de/en/). The programme covers fish sampling at 16 river sites (Figure 5) and one lake (Lake Belau, Northern Germany; this lake is considered as a reference site with low anthropogenic inputs). Sites shortly downstream of large STPs (see section 4.3.3; Subedi et al. 2012) are, e.g., Blankenese (E5 in Figure 5), Weil (R1) or Güdingen (S1).

The archived fish samples (common bream, *Abramis brama*) are available for retrospective monitoring studies. The ESB archive covers time series going back to the early 1990s. In earlier investigations clorophene, triclosan and methyltriclosan were detected in fish samples collected according to the German ESB protocols (Boehmer et al. 2004; Rüdel et al. 2013). The study confirmed earlier findings of methyltriclosan residues in fish from freshwaters reported for Switzerland (Balmer et al. 2004).

Beside fish also mussel samples are available from the German ESB (zebra mussels, *Dreissena polymorpha*). However, up to now only a few retrospective studies have been performed with mussels. Currently approved biocides were not covered yet.

Table 21: Overview of the biocide monitoring proposal for limnic aquatic biota. Monitoring approach: survey.

Criterion	Specification	Comment
Matrix	Fish (or mussels)	According to WFD requirements some compounds are considered for monitoring in biota; thus biota samples may be available from certain programmes which could also be used for a biocides monitoring; archived fish samples are available from Environmental Specimen Banks
Relevant PTs and typical substances	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 from direct inputs; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via STPs	Examples for detected compounds: triclosan (PT 1, 2, 7, 9) and its TP methyltriclosan; refer to Table 23 for prioritised compounds
Monitoring approach	Survey: annual sampling of several fish from each site (WFD surveillance monitoring, WFD trend monitoring)	Analysis of individual fish or preparation of a pooled sample for analysis; use of liver or muscle tissue (depending on internal distributions of target compounds in fish), or whole fish
Scale of monitoring	National scale	In larger rivers and lakes (depends on the availability of appropriate biota samples)
Relevant sites	Larger rivers and lakes	Sites in urban regions and those influenced by STP effluents seem most appropriate (potential exposure of fish)
Relevant monitoring programmes in Germany/ Europe	WFD compliance monitoring (in Germany already performed by some federal states); German Environmental Specimen Bank; Swedish Environmental Specimen Bank	Archived fish samples from Environmental Specimen Banks allow a retrospective monitoring (see example for Lindane fish residues in Figure 7)
	UK Fish Tissue Archive	Source: Jürgens et al. (2013); www.ceh.ac.uk/sci_programmes/water/nationalfishtissuearchive.html
	Swedish Monitoring Program	Gustavsson et al. (2010)

Criterion	Specification	Comment
Appropriate sampling methods	Standard operating procedures for the sampling of common bream (*Abramis brama*) and zebra mussel (*Dreissena polymorpha*) are available from the German Environmental Specimen Bank Guidance on chemical monitoring of sediment and biota (EC 2010)	Download of protocols at www.umweltprobenbank.de/en/documents/publications Procedure according to WFD requirements
Appropriate analytical methods	Multi-methods available covering many compounds (however; LOQ may be high); specific methods are available for some compounds (e.g., triclosan and its TP methyltriclosan in fish, Rüdel et al. 2013)	Currently only a few studies are available; in Lower Saxony fish was investigated for a large number of PPP/biocides but without findings above the LOQ (NLWKN 2009)
Limits of detection (LOD) / Limits of quantification (LOQ)	LOD for triclosan and methyltriclosan in fish muscle tissue: 0.20 and 0.25 ng/g wet weight, respectively	Rüdel et al. (2013)
Availability of labelled standard compounds	e.g., standards from CIL, Inc. (in Germany available via LGC Standards, www.lgcstandards.com): triclosan ($^{13}C_{12}$, 99%), methyltriclosan (ring-$^{13}C_{12}$, 99%); from Toronto Research Chemicals (via www.biozol.de): permethrin-D5	Alternative: use of labelled compounds with similar chemical properties or external calibration

Table 22: Examples for available biocide data from the monitoring of limnic aquatic biota.

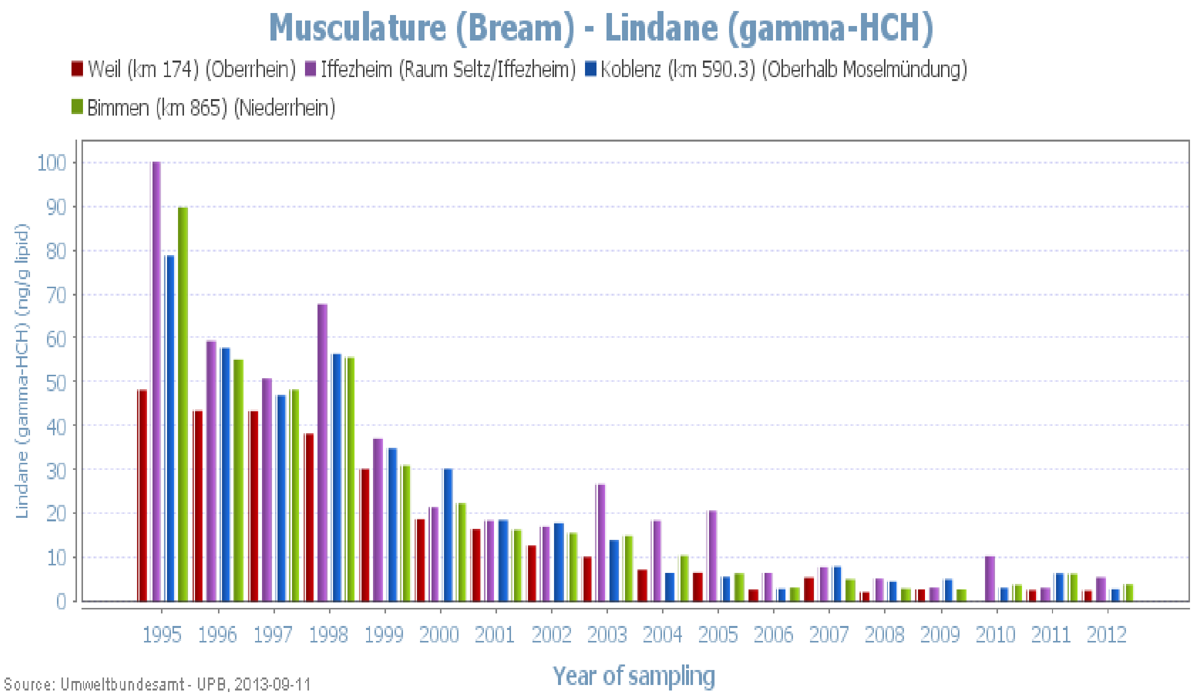
Type of information	Description	Comment/Source
(Online) data sources	Data, e.g., for organotin compounds (banned antifouling compounds), lindane (biocide, not included in review programme) and triclosan/methyltriclosan are available from investigations of the German Environmental Specimen Bank	Data from the German Environmental Specimen Bank can be retrieved at www.umweltprobenbank.de/en/
Literature	Detection of triclosan and its TP methyltriclosan in fish from the German Environmental Specimen Bank	Rüdel et al. (2013

Table 23: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner, 2014): compounds (biocides and transformation products) relevant for monitoring in aquatic biota. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of monitoring in water, BCF › 100, not "readily biodegradable". TOP 10 compounds with relevant PT(s) and without current PPP authorisation.

Ranking Aquatic Biota Compound	CAS no.	PPP (in Germany) authorised until	PT(s) approved / in review programme	BCF [L/kg]	SCORE # Monitoring in water
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	-	7, 8, 9, 10, 11, 21	750	378
Triclosan	3380-34-5	-	1,2,7,9	8700	280
Methyltriclosan (Triclosan TP)	4640-01-1	-	1,2,7,9	18000	224
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	570	162
Chlorfenapyr	122453-73-0	-	8, 18	2140	81
Methyl-DCPP (DCPP TP)	-	-	1, 2, 4	488	75
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	-	18	502	48
Transfluthrin	118712-89-3	-	18	1801	48
Flufenoxuron	101463-69-8	-	8	25000	44
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	-	18	1213	42

PPP - plant protection product. BCF - bioconcentration factor (from EU biocide Assessment reports).
score for the relevance for monitoring the listed compounds in the aquatic environment based on the criteria described in Rüdel and Fliedner (2014). - no data/not assessed.

Figure 7: Monitoring data from the German Environmental Specimen Bank (ESB): time series for concentrations of lindane (biocide, not included in review programme; also former PPP) in bream fillet from four Rhine river sites, period 1995 - 2012. Data are ng/g lipid.



Data source: www.umweltprobenbank.de/en/.

4.4 Monitoring of the terrestrial environment

4.4.1 Soil

Currently only a few data on biocide levels in soil are available. These data mostly refer to compounds which are also used as PPP so that the source of the findings cannot be clearly allocated (e.g., for residues of chlorotoluron, isoproturon, or terbuthylazine; survey of soil monitoring in German federal states, Rüdel and Knopf 2012).

To investigate the relevance of a biocide monitoring in soils a feasibility study (research project) is suggested. Only after the relevance of biocide residues in soil has been proven a broader monitoring seems appropriate. Relevant entries of biocides into soils may occur via manure or slurry (these may contain disinfectants applied in livestock breeding) or agricultural usage of sewage sludge. Another potential pathway of biocides into soil and groundwater is the de-centralised infiltration of rainwater into soil (relevant for compounds used in PT 7, 10 and partly PT 9, i.e. biocides in polymeric roof membranes).

Table 24 gives an overview of the suggested approach for soil monitoring. Examples for information sources on soil monitoring studies are displayed in Table 25. Compounds prioritised for soil monitoring are listed in Table 26.

Table 24: Overview of the biocide monitoring proposal for soil. Monitoring approach: research project.

Criterion	Specification	Comment
Matrix	Soil	Sampling standards should be followed
Relevant PTs and typical substances	PT 7, 8, 10, 14, 18, 19 from direct inputs; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via sewage sludge or slurry/manure	For relevant compounds according to the prioritisation approach refer to Table 26
Monitoring approach	Research project: annual sampling at representative sites	A cooperation with German federal states authorities is proposed for site identification and sampling
Scale of monitoring	Selected sites with expected exposure	A feasibility study is suggested; e.g., investigation of relevant biocides (e.g., disinfectants like triclosan or QAC)
Relevant sites	Selection criteria: sites with nearby biocide use (direct input) Sites with indirect input (slurry/manure, sewage sludge)	Sites in urban regions and those influenced by biocide usage (e.g. sites for wood storage) In regions with land application of sewage sludge or slurry/manure; relevant sites for slurry application may be identified based on results of the UBA-funded project "Antibiotics and parasiticides in groundwater at sites with high livestock density" (FKZ 3711 23 225)
Relevant monitoring programmes in Germany/ Europe	Soil samplings of German federal states (permanent soil investigation sites); German Environmental Specimen Bank: archive of soil samples	German ESB soils samples are less appropriate in this context since mostly forest soils are sampled; sampling only every four years since the year 2002 so that trends can only be detected after long periods
Appropriate sampling methods	Soil sampling standards: ISO 10381-1 (2002), ISO 10381-2 (2002) A standard operating procedure for the sampling of soil is available from the German Environmental Specimen Bank	Source: http://www.umweltprobenbank.de/upb_static/fck/download/SOP_Soil.pdf
Appropriate analytical methods	Information on analytical methods for soil are mostly available in the Doc I-biocide Assessment Reports For some biocides literature sources for soil analytical methods are available	The Assessment Reports contain mostly no detailed descriptions; more information may be provided in not freely available Annexes Chitescu et al. (2012): HPLC-MS screening method for fungicides in soil samples Flores-Ramírez et al. (2012): analytical method for Fipronil and its degradation products in soil samples Hernández et al. (2013a): simultaneous de-

Criterion	Specification	Comment
		termination of nine anticoagulant rodenticides in soil by HPLC-MS
Limits of detection (LOD) / Limits of quantification (LOQ)	The method should at least allow to analyse the compliance with the PNECsoil of the respective compounds (LOQ at 30% of the respective PNEC value) The Doc I-biocide Assessment Reports for relevant compounds should be checked for specific analytical method information For the compounds identified as relevant (Table 26) no literature source for LOD/LOQ data for soil could be retrieved	For DDAC a LOQ of 0.01 µg/g is given for a LC-MS method (not specified) in one Doc I-biocide assessment report (PNECsoil = 0.281 µg/g wet weight); however, the method was assessed as not sufficiently validated In another Doc I-biocide Assessment Report for DDAC a LOQ of 0.05 µg/g is given (also for a LC-MS method); the derived PNECsoil was in this report given as 0.01 mg/g wet weight; thus the method would not be sufficient for analysis in the range of the PNEC
Availability of labelled standard compounds	e.g., standards from CIL, Inc. (in Germany available via LGC Standards GmbH, Wesel; www.lgcstandards.com): available standards for compounds listed in Table 26: cis-permethrin (phenoxy-13C6, 99%), trans-permethrin (phenoxy-13C6,99%), trans-cyfluthrin-D6 (2,2-dimethyl-D6)	Labelled standards are mainly available for compounds also used as PPP

Table 25: Examples for available biocide data from the monitoring of soil.

Type of information	Description	Comment/Source
Literature	Only few reports with relevant soil residue data for relevant compounds are available, mostly residues from agricultural sources (for biocides also used as PPP)	
	HPLC-MS screening method for fungicides in soil samples (included thiabendazole, propiconazole, tebuconazole, cyproconazole, carbendazim; no relevant compound detected in a screening study in the Netherlands	Chitescu et al. (2012)
	Simultaneous determination of nine anticoagulant rodenticides in soil, bromadiolone and chlorophacinone were found in very low concentrations in, respectively, three (‹ LOQ, 3 and 6 µg/kg) and two (‹ LOQ, and 5 mg/kg) samples of a set of 60 soil samples tested	Hernández et al. (2013a)
	Data on triclosan residues in Swedish soils, range ‹ LOD - 15 µg/g dry weight (n = 7)	Nordic Council (2012)

Table 26: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for monitoring in soil. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of terrestrial monitoring, K_{OC} › 10000, not "readily biodegradable", TOP 10 compounds with relevant PT(s) and without current PPP authorisation.

Ranking SOIL Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	K_{OC} [L/kg]	Persistence (as score) §	SCORE # Terrestrial monitoring
Didecyldimethylammonium chloride (DDAC)	7173-51-5	-	1, 2, 3, 4, 6, 8, 10, 11, 12	1018685	1	240
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	76900	3	216
Didecylmethylpoly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	-	2, 4, 8, 9, 10, 11, 12	1103802	4	150
Chlorfenapyr	122453-73-0	-	8, 18	11960	3	108
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	-	18	35171	2	72
Transfluthrin	118712-89-3	-	18	53703	3	72
d-Phenothrin	26046-85-5	-	18	125893	5	63
Cyfluthrin	68359-37-5	2009	18	123930	4	60
Pyriproxyfen	95737-68-1	-	18	21175	2	54
Hexaflumuron	86479-06-3	-	18	22133	5	54

K_{OC} - soil organic carbon-water partitioning coefficient (from EU biocide Assessment reports). § score from 0 = readily biodegradable to 5 = very persistent. # score for the relevance for monitoring the listed compounds in the terrestrial environment based on the criteria described in Rüdel and Fliedner (2014).

4.4.2 Terrestrial biota

A monitoring in terrestrial biota (soil fauna) may be considered for compounds which have a bioaccumulative potential and are emitted directly or indirectly to soils. Raptors are covered in section 4.2.

Monitoring programmes for terrestrial biota are scarce. In Germany, mainly the German Environmental Specimen Bank provides a systematic approach. From the species covered in principle earthworm, roe deer (liver), and feral pigeon (eggs) could be relevant (other species are trees which seem not relevant in this context). However, many of the terrestrial ESB sampling sites are in regions with low anthropogenic impacts (e.g., national parks or biosphere reserves), and an exposure to biocides seems unlikely. Nevertheless, in some ESB forest sampling areas wood preservatives may be applied occasionally for temporarily wood storage. In such scenarios biocide residues may also be taken up by terrestrial biota.

The biocides which may be relevant for a monitoring in terrestrial biota were identified by a prioritisation scheme (Rüdel and Fliedner 2014). As proxy for the bioaccumulation potential of compounds in terrestrial ecosystems the bioconcentration factor for fish was chosen since only a few data on bioaccumulation in terrestrial organisms are available (i.e. in the EU biocide Assessment Reports for most compounds no data for the BCF in earthworms are given or only calculated data are provided). The BCF (fish) threshold value applied for the prioritisation is 2000 L/kg.

The proposal for monitoring biocides in terrestrial biota is shown in Table 27, and Table 28 gives examples for available information sources for monitoring data for this scenario. Compounds prioritised for monitoring in soil biota are listed in Table 29.

Table 27: Overview of the biocide monitoring proposal for terrestrial biota. Monitoring approach: research project.

Criterion	Specification	Comment
Matrix	Soil organisms	e.g., earthworms, rodents
Relevant PTs and typical substances	PT 7, 8, 10, 14, 18, 19 from direct inputs; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via sewage sludge or slurry/manure	See list from prioritisation approach in Table 29
Monitoring approach	Research project: single samplings of potentially exposed sites	For biota a single sampling should be considered; examples are the sampling schedules for terrestrial biota (e.g., earthworm, roe deer liver, feral pigeon eggs) of the German Environmental Specimen Bank; retrospective study with archived samples possible
Scale of monitoring	Selected sites	A feasibility study is suggested; e.g., investigation of slurry/sewage sludge treated soils for relevant biocides (e.g., disinfectants like triclosan, veterinary biocides)
Relevant sites	Selection criteria: sites with (potential) nearby biocide use (direct input)	Sites in urban regions and those influenced by biocide usage (e.g., sites for wood storage); near farm buildings and in suburban areas

Criterion	Specification	Comment
	Sites with indirect input (slurry/manure, sewage sludge)	In regions with land application of sewage sludge or slurry/manure
Relevant monitoring programmes in Germany/ Europe	Archived terrestrial biota samples (e.g., earthworm samples) from the German Environmental Specimen Bank	German ESB sites may be less appropriate in this context since mostly forest soils are sampled (no inputs via sewage sludge or slurry/manure); a specific programme may be required
Appropriate sampling methods	Standard operating procedures for the sampling of earthworm, roe deer liver, feral pigeon eggs are available from the German Environmental Specimen Bank Sampling procedure for earthworm for passive biomonitoring	Source: www.umweltprobenbank.de/en/documents/publications VDI 4230-2 (2008)
Appropriate analytical methods	Method information for residue analysis in organisms and/or tissues are available in the Doc I-biocide Assessment Reports, if an exposure is assumed as relevant (but mostly no detailed method description provided)	For terrestrial biota analytical methods for rodenticides are available (e.g., Hernández et al. 2013b, analysis of vole tissue) Generally methods from aquatic biota applications can often be adapted to terrestrial biota
Limits of detection (LOD) / Limits of quantification (LOQ)	LOQ 0.6 - 4.6 µg/kg for chlorophacinone, bromadiolone, brodifacoum and difenacoum in common vole tissues	Hernández et al. (2013b)
Availability of labelled standard compounds	e.g. standards from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; in Germany available via LGC Standards GmbH, Wesel): from the compounds listed in Table 29 only triclosan ($^{13}C_{12}$, 99%) and methyl-triclosan (ring-$^{13}C_{12}$, 99%) are available	

Table 28: Examples for available biocide data from the monitoring of terrestrial biota.

Type of information	Description	Comment/Source
(Online) data sources	UK Wildlife Disease and Contaminant Monitoring and Surveillance network	Source: https://wiki.ceh.ac.uk/display/wildcomsweb/Home (annual reports and thematic reports available for downloading)
Literature	Analysis of anticoagulant rodenticide residues in vole (*Microtus arvalis*) tissues	Hernández et al. (2013b)

Type of information	Description	Comment/Source
	Primary and secondary poisoning by anti-coagulant rodenticides of non-target animals in Spain, SGAR levels were studied in liver of 401 wild and domestic animals found dead in Spain with evidences of poisoning, including 2 species of reptiles (n=2), 42 species of birds (n=271) and 18 species of mammals (n=128)	Sánchez-Barbudo et al. (2012)

Table 29: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for soil biota. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of terrestrial monitoring, BCF (fish) › 2000, not "readily biodegradable", all compounds with relevant PT(s) and without current PPP authorisation.

Ranking TERRESTRIAL BIOTA Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	BCF (fish) $	Persistence (as score) §	SCORE # Terrestrial monitoring
Triclosan	3380-34-5	Keine	1,2,7,9	8700	5	280
Methyltriclosan (Triclosan TP)	4640-01-1	-	1,2,7,9	18000	5	224
Chlorfenapyr	122453-73-0	-	8, 18	2140	3	108
Hexaflumuron	86479-06-3	-	18	5600	5	54
Flufenoxuron	101463-69-8	-	8	25000	5	44
Creosote	8001-58-9	-	8	5000	4	40
Flocoumafen	90035-08-8	2003	14	36134	5	30
Difethialone	104653-34-1	2004	14	40000	5	30
Brodifacoum	56073-10-0	2010	14	35134	4	27
urea metabolite (Flufenoxuron TP)	-	-	8	25000	2	24

PPP - plant protection product. BCF - bioconcentration factor. § score from 0 = readily biodegradable to 5 = very persistent. # score for the relevance for monitoring the listed compounds in the terrestrial environment biota based on the criteria described in Rüdel and Fliedner (2014). $ BCF for fish was chosen since BCF for terrestrial organisms were not available for most compounds in the data set (based on EU biocide Assessment reports).

4.4.3 Ground water

After entry of biocides into soils (see above), there may also be a possible discharge into the groundwater. The scenario applied here is the direct entry of biocides into soils. Currently, these considerations do not cover bank filtration, i.e. the use of surface water for groundwater enrichment. For the bank filtration scenario other criteria for prioritisation would apply (e.g., biocides with relevance for surface waters which have a certain persistence and mobility in soil).

Routinely, groundwater investigations are performed in the context of general environmental monitoring and the monitoring of raw water for drinking water production. The UBA operates a database for geodata-based evaluations of positive findings in monitoring programmes reported to the UBA (Karl et al 2013). This databank allows a Germany-wide spatial and temporal analysis of the risk to groundwater and allows the derivation of assessment strategies and decision criteria. The databank was implemented for PPP findings in groundwater (these include PPP also authorised as biocides). However, the approach may be extended for the use with biocides (additional compounds, coverage of non-agricultural regions).

A procedure for the performance of specific groundwater monitoring studies is described by Aden et al. (2002). It was developed for the performance of post-authorisation studies on PPP but the general outline is also applicable to groundwater monitoring studies of biocides.

Table 30 presents a proposal for biocide monitoring in groundwater and Table 31 shows some information sources for groundwater monitoring data. To assess the possible entry of biocides into groundwater, mobility in soil is considered in the prioritisation scheme for this scenario (Rüdel and Fliedner 2014). The list of biocides selected in this procedure is presented in Table 32.

Table 30: Overview of the biocide monitoring proposal for groundwater. Monitoring approach: screening.

Criterion	Specification	Comment
Matrix	Groundwater	It is proposed to cooperate with institutions responsible for the groundwater monitoring according to WFD obligations
Relevant PTs and typical substances	PT 7, 8, 10, 14, 18, 19 from direct inputs to the soil; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via sewage sludge or slurry/manure to the soil	Current findings in groundwater are not clearly allocable to biocide usage (may also be caused by PPP use); relevant compounds according to the prioritisation scheme are given in Table 32
Monitoring approach	Screening: several samplings per year	Use of appropriate wells

Criterion	Specification	Comment
Scale of monitoring	Selected sites (groundwater wells) with expected exposure, depending on the focus: To cover the direct entry of biocides into soils To cover the indirect entry of biocides into soils	 Sampling in urban regions / regions without agricultural use of the potential target compounds Sampling in urban regions with decentralised infiltration of rainwater into soil; Sampling in agricultural areas with slurry/sludge application (limited to compounds that have not been authorised as PPP)
Relevant sites	Sites with nearby biocide use (direct input), as screening study Sites with indirect input (slurry/manure, sewage sludge), as research project	Sites in urban regions and those influenced by biocide usage (e.g. sites for wood storage) In regions with land application of sewage sludge or slurry/manure
Relevant monitoring programmes in Germany/ Europe	The UBA operates a database of findings of PPP/biocidal compounds in groundwater (UBA sections II 2.1, IV 1.3)	
Appropriate sampling methods	For groundwater sampling standard methods are available (mostly international standards), e.g. : design of sampling programmes, ISO 5667-1 (2006); guidance on groundwater sampling, ISO 5667-11 (2009); preservation and handling of water samples, ISO 5667-3 (2012); quality assurance and quality control, ISO 5667-14 (2013)	A collaboration with water supply companies operating wells is recommended
Appropriate analytical methods	Available analytical methods for surface water monitoring can be applied (see Table 11)	
Limits of detection (LOD) / Limits of quantification (LOQ)	-	LOD requirement: 0.03 µg/L (to allow a compliance testing with groundwater concentrations of $<$ 0.1 µg/L, the threshold value for individual PPP/biocide substances in drinking water according to the European Drinking Water Directive 98/83/EC)
Availability of labelled standard compounds	No labelled standards for the compounds prioritised in Table 32 could be retrieved	

Table 31: Examples for available biocide data from the monitoring of for groundwater.

Type of information	Description	Comment/Source
(Online) data sources	Some German federal states operate online databases for ground water monitoring data The Netherlands operate a database on pesticide monitoring data in surface waters	Source: e.g., for Baden-Wuerttemberg http://193.197.158.205/servlet/is/200/; relevant data are mainly for biocides also applied as PPP Source: http://www.bestrijdingsmiddelenatlas.nl/atlas.aspx
Literature	Evaluation of German groundwater monitoring data	Report for Germany: Wasserwirtschaft in Deutschland, Teil Gewässergüte (Arle et al. 2010); mostly for biocides also used as PPPs

Table 32: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for groundwater. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of terrestrial monitoring, GUS › 2.8, all compounds from the data set with relevant PT(s) and without current PPP authorisation.

Ranking GROUNDWATER Compound	CAS no.	PPP (in Germany) authorised until	PT(s) approved / in review programme	GUS (as score) §	SCORE # Terrestrial monitoring
DMSA (Dichlofluanid TP)	4710-17-2	2003	7, 8, 21	4.3	72
MITC (Dazomet TP)	556-61-6	2004	6, 8, 12	3.7	72
C(M)IT (5-chloro-2-methyl-4-isothiazolin-3-one)	26172-55-4	-	2, 4, 6, 11, 12, 13	3.4	63
Fipronil	120068-37-3	-	18	2.9	54
MIT (2-methyl-4-isothiazolin-3-one)	2682-20-4	-	2, 4, 6, 11, 12, 13	4.7	54
FPB-acid (Cyfluthrin TP)	-	2009	18	4.0	24
Sodium Warfarin	129-06-6	1974	14	3.3	16
Permethric acid (Cyfluthrin TP)	-	2009	18	4.2	12
Warfarin	81-81-2	2012	14	3.3	8

PPP - plant protection product. GUS - Groundwater Ubiquity Score (calculated according to Gustafson 1989 on base of data from the EU biocide Assessment reports). # score for the relevance for monitoring the listed compounds in the terrestrial environment based on the criteria described in Rüdel and Fliedner (2014).
- no data/not relevant.

The study by TZW (2012) also lists biocides with relevance for groundwater. Similar to the approach outlined in Rüdel and Fliedner (2014), the prioritisation considered usage patterns on basis of the study by COWI (2009) and aspects of soil mobility (operationalised as water solubility) and degradability (readily biodegradable compounds were considered as not relevant). 24 compounds were selected by TZW (2012), e.g., thiabendazole, cyanamid, MITC (dazomet TP), tolylfluanid, dichlofluanid, MIT, coumatetralyl or imiprothrin (here only examples are listed which are still in the BPD review programme or already included in the list of approved substances according to the BPR, and which are currently not authorised as PPP). Comparison between the TZW- and the present study reveals that only MITC and MIT were selected by both (without consideration of PPP authorised substances; eight compounds of the TZW set could not be considered here because no EU biocide Assessment Report was available).

4.5 Monitoring of the atmosphere

Currently only a few monitoring data for concentrations of authorised biocides in air or airborne particulate matter are available. In most cases the data relate to biocides which are also authorised as PPP. For PPP atmospheric residues may be caused by the usage pattern (spray drift during application or volatilisation from plant and/or soil surfaces after application). Coscollà et al. (2011), e.g., reported on 18 out of a set of 40 pesticides investigated which were detected in airborne particulate matter sampled at a rural site near Valencia in Spain (including compounds also (previously) authorised as biocides as bifenthrin, chlorthalonil, diazinon or fipronil). The limit of quantification (LOQ) ranged from about 1 to 40 pg/m^3 and the detected concentrations ranged from about 1 to 630 pg/m^3. However, it is assumed that the residues detected stem mainly from the PPP use of the detected substances.

In Sweden Palm Cousins et al. (2012) conducted a study to prioritise chemicals for the national long-term air monitoring programme. The approach is based on already existing monitoring data in air and deposition and combines empirical data on occurrence with publicly available quantitative structure activity relationship estimation tools that predict atmospheric persistence and bioaccumulation. None of the compounds prioritised for atmospheric monitoring (e.g., perfluorooctane sulfonate, hexabromocyclododecane and hexachlorobenzene) is currently authorised as biocide. This approach, however, bears a flaw since only compounds which are already monitored enter the prioritisation process while new compounds are excluded. Kördel et al (2013) called such approaches “vicious circles” in which substances are not monitored, because little is known about their occurrence, because they are not monitored, and so forth.

One further air monitoring study from Sweden was conducted on the (non-PPP) biocide triclosan (Dye et al. 2007). At urban Swedish sites triclosan levels of 0.01 - 0.17 ng/m^3 were found whereas the Swedish ambient air levels were 0.003 - 0.005 ng/m^3 (year ca. 2000). The respective particulate matter deposition levels were 9.7 - 20 ng/m^2/d (year ca. 2002) in Swedish urban air and 0.2 - 0.41 ng/m^2/d (year ca. 2002) and 1.6 - 3.5 ng/m^2/d (year ca. 2006; Remberger et al. 2006) in Swedish ambient air. The relevance of the data was not discussed in the report by Dye et al. (2007). In the study by Remberger et al. (2006) in Sweden the atmosphere was identified as a possible transport matrix for triclosan and 2-mercaptobenzothiazole (a former biocide which was not considered for the EU biocides review programme).

Here it is proposed that a monitoring of the atmosphere should be considered for biocides with a vapour pressure of > 0.01 Pa (or a Henry's Law Constant > 0.03 Pa m^3 mol^{-1}) and an atmospheric half-life of > 2 days that are emitted into the air.

Important aspects for the implementation of a monitoring of biocides in the atmosphere are presented in Table 33. Compounds identified as relevant for this monitoring approach are displayed in Table 34.

Table 33: Overview of the biocide monitoring proposal for the atmosphere. Monitoring approach: research project.

Criterion	Specification	Comment
Matrix	air, dry and wet deposition	
Relevant PTs and typical substances	PT 8, 11, 14, 18	Triclosan was identified in air samples in Sweden; relevant compounds as identified in the prioritisation scheme are listed in Table 34
Monitoring approach	Research project: several samplings at selected sites	Because only little information is available relevant scenarios should be monitored in a research study
Scale of monitoring	Selected sites	Scenario with relevant exposure to be identified
Relevant sites	Sites with nearby biocide use	Sites in urban regions and those influenced by biocide usage
Relevant monitoring programmes in Germany/Europe	-	Up to now no monitoring of biocides in the atmosphere (only single measurements)
Appropriate sampling methods	Depends on chemical and fraction to be sampled; e.g., DIN 19739-1 (2002): for measurement of atmospheric deposition of organic trace substances	
Appropriate analytical methods	Refer to EU biocide Assessment Reports	
Limits of detection (LOD) / Limits of quantification (LOQ)	-	
Availability of labelled standard compounds	For the compounds selected as relevant for monitoring in the atmosphere (Table 34) no labelled compounds could be retrieved	Alternative: use of labelled compounds with similar chemical properties or external calibration

Table 34: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for monitoring in the atmosphere. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of monitoring in the atmosphere, vapour pressure › 0.01 Pa or Henry's Law-Constant › 0.03 Pa m^3 / mol, atmospheric half-life › 2 days, all relevant compounds from the data set with relevant PT(s) and without current PPP authorisation.

Ranking Atmosphere Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	Henry's Law-Constant [Pa m^3 / mol]	Vapour pressure [Pa]	Half-life [d]	SCORE # Monitoring atmosphere
Hydrogen cyanide	74-90-8	2001	8, 14, 18	8.40 E+04	5.10 E+03	535	108
Methyliso-thiocyanate (MITC) (Dazomet TP)	556-61-6	2004	6, 8, 12	2.50 E+03	2.20 E+01	4.5	36
Transfluthrin	118712-89-3	-	18	1.00 E-04	6.50 E-01	2.4	24
Naled	300-76-5	1976	(18)	3.90 E-02	7.43 E-03	2.5	15
Cyanamide	420-04-2	2001	3, 18	5.10 E-01	2.68 E-05	3.4	10

PPP - plant protection product. # score for the relevance for monitoring the listed compounds in the atmosphere based on the criteria described in Rüdel and Fliedner (2014).

4.6 Monitoring of stormwater and sewage treatment plants

In industrialised countries major inputs into the environment occur via the wastewater path by sewage treatment plants (STP). Biocides from household and other uses are often disposed via the wastewater. Thus a monitoring of relevant fractions in sewage treatment plants should be considered for biocides applied in relevant PT(s).

However, it is also important to consider precipitation management in urban regions and settlements since stormwater (rainwater run-off from buildings and surfaces) may also contain biocides (e.g., from facades or treated areas). If the stormwater is disposed without treatment biocides may reach surface waters without the possibility of elimination in STPs. New sewer systems in Germany are usually carrying household sewage to STPs without gathering stormwater. However, combined sewers are also still in use (about 43% of total sewer length in 2010 were combined sewers, about 36% separate wastewater sewers and about 22% stormwater sewers). There are large regional differences: e.g., in 2007 about 92% of the population in the federal state of Saarland was connected to separate sewer system, but only about 4% in the federal state of Brandenburg (Brombach 2010).

Depending on the question to be dealt with different fractions of a STP may be relevant for a biocide monitoring. The influent fraction (may include stormwater) gives information on the biocides used and the amount in the drained area. The effluent monitoring allows the assessment which biocides are applied and which amounts of these enter surface waters. The difference between both is a measure of the elimination efficiency of STPs (degradation and adsorption to sludge). Finally, the sludge fraction gives information which amount of biocides may reach the food chain (if the sludge is applied to agricultural soils, a practice still common in the Northern part of Germany).

Recently, research studies on the occurrence of biocides in stormwater were performed. Bollmann et al. (2014) investigated levels of biocides used in façade materials or coatings in a Danish urban area. A sampling campaign was conducted over a period of nine month and single rain events were investigated. Highest median concentrations of 45 and 52 µg/L were detected for terbutryne and carbendazim, while the concentrations for, e.g., isoproturon, diuron, OIT, BIT, cybutryne (Irgarol), propiconazole and tebuconazole were lower by factors of about 10. The study also allowed calculating mass flows of biocides.

In a comprehensive study in a small mixed land-use catchment in Switzerland Wittmer et al. (2011) tried to relate the loads of biocide and pesticide residues in surface waters to their respective urban and agricultural usage. The investigation also included a STP, a combined sewer overflow and a stormwater sewer within the area. In the study period rain events were sampled at high temporal resolution. Furthermore, information on the use of biocide and pesticide products were gathered (e.g., by surveys of farmers and private households). Surprisingly, Wittmer et al. (2011) found out that urban biocides, although used in lower amounts, contributed to the total surface water loads in the same range as the more widely-used agricultural pesticides. Obviously the lower use was compensated by higher loss rates in urban areas as compared to those in agricultural land use.

Experiences from sewage sludge monitoring were discussed at a workshop in 2009 (Rüdel et al. 2010). During the workshop it was discussed whether a long-term archiving of sewage sludge in the German Environmental Specimen Bank (ESB) would be feasible. In Sweden such an approach has already been successfully implemented into the ESB concept (Olofsson et al. 2012).

In Germany, emissions from STPs are monitored in the context of self-surveillance by STP operators. Authorities survey emissions only by random control. Monitoring data for STP are only partly published (mostly only sludge levels for regulated compounds or data from research projects) since operators of STPs are often private companies. In many cases it is also difficult to get allowances for STP investigations (in some cases it has to be agreed upon to publish data only without reference to a specific plant).

4.6.1 Influents and effluents of sewage treatment plants

The monitoring approach for influents and effluents of STPs is similar. Often, both sample types are taken in order to follow elimination of target compounds during the treatment process (e.g., investigation by Bester et al. (2003) on triclosan or Luft et al. (2014) on terbutryne and cybutryne/Irgarol).

Important aspects for the performance of a monitoring of influents and effluents of STPs are listed in Table 35. Exemplary sources for data on biocide levels in influents and effluents are given in Table 36, and Table 37 lists the biocides identified as most relevant for the monitoring in STP influents and effluents.

Table 35: Overview of the biocide monitoring proposal for influents and effluents of sewage treatment plants.
Monitoring approach: survey.

Criterion	Specification	Comment
Matrix	Influents and/or effluents of sewage treatment plants	
Relevant PTs and typical substances	PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19	Numerous compounds have been identified in STP influent and effluent samples; relevant compounds as identified by the prioritisation scheme are listed in Table 37
Monitoring approach	Survey: 2 - 4 samplings per year, pooled samples over a period of 24 h (e.g. derived from sub-samples taken in 5 - 30 intervals by an autosampler) For certain investigations it may also be appropriate to take 24 h pool samples as described above over a period of one week or even longer	Sampling in different seasons to identify seasonal effects (e.g., in winter lower concentrations of biocides also applied as PPP) By investigating samples from several days usage pattern can be identified, e.g., lower levels at weekends
Scale of monitoring	Selected STPs sites (collaboration with plant operators and/or federal state authorities); different STP size classes should be covered	A feasibility study is suggested; e.g., investigation of a selected number of influents and effluents of STPs in urban areas
Relevant sites	Sewage treatment plants of differrent size	STPs in urban and rural regions; STP with industrial wastewater
Relevant monitoring programmes in Germany/ Europe	Self-surveillance by STP operators	Mostly no direct reporting
Appropriate sampling methods	Wastewater sampling according to German standard DIN 38402-11 (2009), ISO 5667-14 (2013) for quality assurance and quality control of environmental water sampling and handling	See also discussion in Ort et al. (2010) regarding operation of sampling devices in time- or flow-proportional sampling modes with adequate sampling intervals
Appropriate analytical methods	Wick et al. (2010), Morasch et al. (2010)	Multi-methods covering about 25 biocides (beside other compounds)
Limits of detection (LOD) / Limits of quantification (LOQ)	5 - 100 ng/L in influents, 2.5 - 50 ng/L in effluents (Wick et al. 2010), 4 - 130 ng/L in influents, 1 - 33 ng/L in effluents (Morasch et al. 2010)	Partly high LOQ due to multi-method (compromise conditions to cover as much compounds as possible)

Criterion	Specification	Comment
Availability of labelled standard compounds	e.g. standards from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; in Germany available via LGC Standards GmbH, Wesel): triclosan ($^{13}C_{12}$, 99%), methyltriclosan (ring-$^{13}C_{12}$, 99%) e.g. PESTANAL standards from Sigma-Aldrich: isoproturon-D6; e.g. standards from Dr. Ehrenstorfer: propiconazole D5 (2,2,3,3,3-propyl-D5), tebuconazole D6 (ethylen D4, methylen D2) e.g., standards from Toronto Research Chemicals, in Germany available via BIOZOL Diagnostica Vertrieb GmbH, Eching): Irgarol-D9	

Table 36: Examples for available biocide data from the monitoring of influents and effluents of sewage treatment plants.

Type of information	Description	Comment/Source
(Online) data sources	Data from effluents of STPs are reported via the Pollutant Release and Transfer Register (PRTR); coverage of about 70 compounds including some biocides	Source: www.thru.de/search/ (data for Germany), e.g. data for annual emissions of diuron, isoproturon, naphthalene and some no-longer approved biocides from STPs
Literature (examples)	Detection of, e.g., diuron, isoproturon, carbendazim, terbutryne, cybutryne (Irgarol)	Wick et al. (2010)
	Target analysis for terbutryne, cybutryne (Irgarol) and several transformation products	Luft et al. (2014)
	EU-wide monitoring survey on polar organic contaminants in STP effluents (including some biocides, e.g., triclosan, isoproturon, chlorotoluron)	Loos et al. (2013)
	Determination of selected QAC by LC-MS in influents and effluents of STPs in Austria	Martínez-Carballo et al. (2007a)

Table 37: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for monitoring of effluents (and influents) of sewage treatment plants. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of STP monitoring, TOP 10 compounds without current PPP authorisation.

Ranking STP EFFLUENTS Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	K_{OC} [L/kg]	Persis-tence (as score) §	SCORE # STP monitoring
Triclosan	3380-34-5	-	1,2,7,9	832	5	210
4,5-Dichloro-2-octyl-2H-iso-thiazol-3-one (DCOIT)	64359-81-5	-	7, 8, 9, 10, 11, 21	6610	2	189
Methyltriclo-san (Triclosan TP)	4640-01-1	-	1,2,7,9	417	5	168
1,2-Benziso-thiazolin-3(2H)-one (BIT)	2634-33-5	-	2, 6, 9, 11, 12, 13	104	3	168
Alkyldimethyl-benzylammo-nium chloride (ADBAC)	68424-85-1	-	1, 2, 3, 4, 6, 8, 10, 11, 12, 13	2658608	0	144
N-(3-aminopro-pyl)-N-dodecyl-propane-1,3-diamine (Lonzabac 12)	2372-82-9	-	2, 3, 4, 6, 8, 11, 12, 13	316228	0	126
3-Iodo-2-pro-pynyl butyl carbamate (IPBC)	55406-53-6	-	6, 7, 8, 9, 10, 12, 13	135	2	120
Didecyldime-thylammonium chloride (DDAC)	7173-51-5	-	1, 2, 3, 4, 6, 8, 10, 11, 12	1018685	1	120
NNOMA (DCOIT-TP) N-(n-octyl) malo-namic acid	-	-	7, 8, 9, 10, 11, 21	-	1	105

Ranking STP EFFLUENTS Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	K_{OC} [L/kg]	Persis-tence (as score) §	SCORE # STP monitoring
Didecylmethyl-poly(oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	-	2, 4, 8, 9, 10, 11, 12	1103802	4	90

K_{OC} - soil organic carbon-water partitioning coefficient (from EU biocide Assessment reports). PPP - plant protection product. § score from 0 = readily biodegradable to 5 = very persistent. # score for the relevance for a monitoring of the listed compounds in STP matrices based on the criteria described in Rüdel and Fliedner (2014).

4.6.2 Sewage sludge

Experiences from sludge monitoring programmes revealed that most pollutants exhibited only small temporal variations in their levels. The characteristics of an STP catchment area, the applied STP technology, or the kind of sludge treatment process had only little influence on the pollutants' burden of the sludge. On the other hand, for some compounds, it was obvious that the procedure of sludge stabilisation (aerobic/ anaerobic) is an important determining factor for pollutants' levels (results of a study by LANUV in the German federal state of North Rhine Westphalia as cited in Rüdel et al. 2010). Investigations in the German federal state of Baden-Wuerttemberg demonstrated the presence of biocides such as terbutryne and propiconazole in sludge. A large-scale sludge monitoring in Switzerland showed that sludge contains a multiplicity of pollutants and is a suitable matrix for the observation of anthropogenic emissions (as documented in Rüdel and Weinfurtner 2009).

The suggested monitoring approach for STP sludge is presented in Table 38 and examples for available data sources for biocide levels in sludge are listed in Table 39. Compounds derived from the prioritisation approach are displayed in Table 40. The two highest ranked compounds are quaternary ammonium compounds (QAC). Several QAC were recently detected in sewage sludge in China (Ruan et al. 2014).

Since the year 2006 the German federal state of North Rhine Westphalia systematically investigates levels of perfluorinated compounds in sewage sludge (LANUV 2014). A similar programme is operated in the federal state of Bavaria for sewage sludge with intended use in agriculture or landscape construction (annual sampling and analysis of sludge; LfU 2014). Since several German federal states operate similar monitoring programmes for STP sludge, it is suggested to ask the operating institutions if relevant biocides can be included in the analysis (as a first step in a survey with the focus on STPs in urban regions).

Table 38: Overview of the biocide monitoring proposal for sewage sludge. Monitoring approach: survey.

Criterion	Specification	Comment
Matrix	Sewage sludge	
Relevant PTs and typical substances	PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19	Numerous compounds have been identified in STP sludge samples; refer to Table 40 for compounds identified as potentially relevant
Monitoring approach	Survey: several samplings per year	
Scale of monitoring	Selected STPs sites (cooperation with plant operators and/or federal state authorities)	A feasibility study is suggested; e.g., investigation of a selected number of STPs in urban areas
Relevant sites	Sewage treatment plants of different size	STPs in urban and rural regions; STP with industrial wastewater
Relevant monitoring programmes in Germany/ Europe	Several German federal states operate monitoring programmes for STP sludge, e.g. North Rhine Westphalia, Bavaria, Baden-Württemberg	
Appropriate sampling methods	International standard for sampling of sludges (ISO 5667-13, 2011); the stabilisation of the sludge after sampling is important (refrigerating to 4°C or freezing; alternatively freeze-drying)	According to the German Sewage Sludge Ordinance (Klärschlamm-verordnung; AbfKlärV 1992) a pooled sample from five time points has to be prepared
Appropriate analytical methods	GC-MS or HPLC-MS methods according to substance properties; partly freeze-dried material is applied	Wick et al. (2010) applied a LC-MS multi-method for biocides including, e.g., diuron, propiconazole, imazalil, carbendazim, terbutryne, cybutryne (Irgarol), M1 (cybutryne TP), BIT, OIT
Limits of detection (LOD) / Limits of quantification (LOQ)	5 - 50 ng/g dry weight (LC-MS/MS method) 100 ng/g dry weight for triclosan (GC-MS method) 2 - 5 ng/g dry weight for QAC (LC-MS/MS method)	Wick et al. (2010) Olofsson et al. (2012) Martínez-Carballo et al. (2014)
Availability of labelled standard compounds	For most of the compounds selected as relevant for monitoring in sludge (Table 40) no labelled compounds could be retrieved; available are permethrin-D5 (from Toronto Research Chemicals via www.biozol.de) and trans-cyfluthrin (2,2-dimethyl-D6) (from LGC Standards (www.lgcstandards.com)	Alternative: use of labelled compounds with similar chemical properties or external calibration; available labelled QAC standards are, e.g., benzyldimethyltetradecylammonium-D7 or benzyldodecyldimethylammonium-D5 (from Toronto Research Chemicals via www.biozol.de)

Table 39: Examples for available biocide data from the monitoring of for sewage sludge.

Type of information	Description	Comment/Source
(Online) data sources	German federal state of Baden-Wuerttemberg: annual reports on levels of chemicals in sewage sludge	Source: www.lubw.baden-wuerttemberg.de/servlet/is/26044/ (reports cover only "classical" pollutants like metals and polychlorinated biphenyls)
Literature	Detection of, e.g., imazalil, propiconazole, carbendazim, terbutryne, cybutryne (Irgarol), BIT, OIT in sludge	Wick et al. (2010)
	Determination of azole compounds in sludge from Spanish STPs by LC-MS/MS	García-Valcárcel and Tadeo (2011)
	In a study in Switzerland the biocides carbendazim, cybutryne (Irgarol) and permethrin were detected in STP sludge (OIT was not detected)	Plagellat et al. (2004)
	Time trend data for triclosan in archived sewage sludge (Swedish Environmental Specimen Bank)	Olofsson et al. (2012)
	Determination of selected QAC by LC-MS in sludge of STPs in Austria	Martínez-Carballo et al. (2007b)
	Analysis of QAC in sludge	Ruan et al. (2014)

Table 40: Results from prioritisation approach (details see report for work package III, Rüdel and Fliedner 2014): compounds (biocides and transformation products) relevant for monitoring of sewage sludge. Selected from a data set of about 130 biocides and 70 transformation products. Criteria: score for relevance of STP monitoring, K_{OC} < 10000, not "readily biodegradable", TOP 10 compounds with relevant PT(s) and without current PPP authorisation.

Ranking SLUDGE Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	K_{OC} [L/kg]	Persistence (as score) §	SCORE # STP monitoring
Didecyldimethyl-ammonium chloride (DDAC)	7173-51-5	-	1, 2, 3, 4, 6, 8, 10, 11, 12	1018685	1	120
Didecylmethyl-poly (oxyethyl) ammonium propionate DMPAP (Bardap 26)	94667-33-1	-	2, 4, 8, 9, 10, 11, 12	1103802	4	90
Permethrin (cis/trans ratio of 25:75)	52645-53-1	-	8, 9, 18	76900	3	54

Ranking SLUDGE Compound	CAS no.	PPP status (in Germany) authorised until	PT(s) approved / in review programme	K_{OC} [L/kg]	Persis-tence (as score) §	SCORE # STP monitoring
(AEM 5772 TP) 3-(trihydroxy-silyl) propyldi-methyloctadecyl ammonium chlo-ride	199111 -50-7	-	2, 7, 9	6370000	2	30
Chlorfenapyr	122453 -73-0	-	8, 18	11960	3	27
Chrysanthemum cinerariaefoli-um, Extract	8003-34-7 / 89997-63-7	-	18	35171	2	24
Transfluthrin	118712 -89-3	-	18	53703	3	24
d-Phenothrin ((1R)-trans phe-nothrin)	26046-85-5	-	18	125893	5	21
Cyfluthrin	68359-37-5	2009	18	123930	4	20
Pyriproxyfen	95737-68-1	-	18	21175	2	18

K_{OC} - soil organic carbon-water partitioning coefficient (from EU biocide Assessment reports). PPP - plant protection product. § score from 0 = readily biodegradable to 5 = very persistent. # score for the relevance for a monitoring of the listed compounds in STP matrices based on the criteria described in Rüdel and Fliedner (2014).

5 Synopsis and discussion

The proposed biocide monitoring approach relies in a first step mainly on cooperation with existing programmes. It is suggested to contact institutions involved in these programmes with proposals to cover additional biocides in their programme. The proposal should contain information on the respective compounds (e.g., use pattern, estimated annual consumption, important properties), information on effect concentrations in the respective compartment (e.g., PNEC for freshwater or soil organisms), information on possible environmental concentrations (e.g., from other European countries) as well as available information on analytical methods.

At least some biocidal compounds may already be covered by programmes (e.g., for surface water monitoring according to WFD obligations). In these cases an evaluation of the compiled monitoring data is proposed.

In some cases samples from environmental specimen banks may be useful. If an analytical method for the respective compound is available, the investigation can be conducted relative quickly. Times series of archived samples can provide fast information on possible trends in environmental concentrations of target compounds. Specimen banks mostly archive biota samples from scheduled sampling campaigns (e.g., fish fillet or mussels), but also soil and suspended particulate matter or in some cases sewage sludge. In some specimen banks also opportunistically sampled material is archived (e.g., tissue from dead-found feral organisms like raptors or otters). Cooperation with these banks seems also a promising approach to gain biocide monitoring data.

All proposed monitoring activities should be organised in a stepwise approach (the availability of appropriate standards and adequate analytical methods with a sufficient low limit of quantification is assumed). Ideally, at first a screening study should be performed to test whether the target compound can be detected in the identified compartment at relevant concentrations. This screening may be performed near to possible sources. If the screening confirms the presence of the compound in the selected compartment the next step should be the performance of a survey in different regions. If the survey confirms the environmental relevance of the target compound (e.g., positive findings with concentrations in the range of the PNEC) these compounds may be proposed for inclusion in the routine monitoring programmes.

Since at the moment EU biocide Assessment Reports are only available for a part of the biocides covered by the EU biocides review programme, the current prioritisation results are only preliminary. They may be revised if EU Assessment Reports for additional biocides become available or if other compounds are removed after non-inclusion decisions are taken (in these cases no Assessment Reports are prepared/published).

6 References

AbfKlärV (1992): Klärschlammverordnung (Sewage Sludge Ordinance). Ordinance of April 15, 1992, lastly amended on February 24, 2012. BGBl. I S. 212.

Aden, K., Binner, R., Fischer, R., Gottschild, D., Kloskowski, R., Schinkel, K., Michalski, B. (2002). Schutz des Grundwassers vor Pflanzenschutzmitteleinträgen: Leitlinie zur Aufklärung von Funden und zur Durchführung von zulassungsbegleitenden Monitoringstudien. Nachrichtenbl. Deut. Pflanzenschutzd. 54, 125-129.

Arle, J., Blondzik, K., Claussen, U., Duffek, A., Heidemeier, J., Hilliges, F., Hoffmann, A., Koch, D., Leujak, W., Mohaupt, V., Naumann, S., Richter, S., Ringeltaube, P., Schilling, P., Schröter-Kermani, C., Ullrich, A., Wellmitz, J., Wolter, R. (2010): Wasserwirtschaft in Deutschland, Teil 2 – Gewässergüte. Umweltbundesamt, Dessau-Roßlau, Stand Juli 2010. http://www.umweltdaten.de/publikationen/fpdf-l/3470.pdf

Arle, J., Blondzik, K., Claussen, U., Duffek, A., Grimm, F., Hilliges, F., Hoffmann, A., Leujak, W., Mohaupt, V., Naumann, S., Pirntke, U., Richter, S., Schilling, P., Schröter-Kermani, C., Ullrich, A., Wellmitz, J., Werner, S., Wolter, R. (2013): Wasserwirtschaft in Deutschland, Teil 2 – Gewässergüte. Umweltbundesamt, Dessau-Roßlau, Stand November 2013. http://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/wawi_teil_02_2014.pdf

Balmer, M. E., Poiger, T., Droz, C., Romanin, K., Bergqvist, P.,-A. Müller, M. D., Buser, H.-R. (2004): Occurrence of Methyl Triclosan, a Transformation Product of the Bactericide Triclosan, in Fish from Various Lakes in Switzerland. Environ. Sci. Technol. 38, 390-395.

Bester, K. (2003): Triclosan in a sewage treatment process - balances and monitoring data. Water Res. 37, 3891-3896.

Bignert, A. (2007): PIA statistical application developed for use by the Arctic Monitoring and Assessment Programme (Trend Analysis Package). Download from www.amap.no.

Boehmer, W., Ruedel, H., Wenzel, A., Schroeter-Kermani, C. (2004): Retrospective Monitoring of Triclosan and Methyl-triclosan in Fish: Results from the German Environmental Specimen Bank. Organohalogen Comp. 66, 1489-1494.

Bollmann, U.E., Vollertsen, J., Carmeliet, J., Bester, K. (2014): Dynamics of biocide emissions from buildings in a suburban stormwater catchment - Concentrations, mass loads and emission processes. Water Res. 56C, 66-76.

Brombach, H. (2010): Im Spiegel der Statistik: Abwasserkanalisation und Regenwasserbehandlung in Deutschland. Korrespondenz Abwasser 57(1), 28-36.

Buerge, I. J., Poiger, T. (2011): Acesulfam: ein künstlicher Süßstoff als Abwasserindikator. Nachr. Chem. 59, 1084-1086.

Burkhardt, M., Zuleeg, S., Vonbank, R., Bester, K., Carmeliet, J., Boller, M., Wangler, T. (2012): Leaching of biocides from façades under natural weather conditions. Environ. Sci. Technol. 46, 5497-5503.

Chitescu, C.L., Oosterink, E., de Jong, J., Stolker, A.A. (2012): Ultrasonic or accelerated solvent extraction followed by U-HPLC-high mass accuracy MS for screening of pharmaceuticals and fungicides in soil and plant samples. Talanta 88, 653-662.

Christensen, T.K., Lassen, P., Elmeros, M. (2012): High exposure rates of anticoagulant rodenticides in predatory bird species in intensively managed landscapes in Denmark. Arch. Environ. Contam. Toxicol. 63, 437-444.

Coscollà, C., Castillo, M., Pastor, A., Yusà V. (2011): Determination of 40 currently used pesticides in airborne particulate matter (PM 10) by microwave-assisted extraction and gas chromatography coupled to triple quadrupole mass spectrometry. Anal. Chim. Acta 693, 72-81.

COWI (2009): Assessment of different options to address risks from the use phase of biocides. Final report on behalf of the European Commission Environment Directorate-General, March 2009. COWI A/S, Kongens Lyngby, Denmark.
http://ec.europa.eu/environment/archives/ppps/pdf/final_report0309.pdf
http://ec.europa.eu/environment/archives/ppps/pdf/annex1.pdf
http://ec.europa.eu/environment/archives/ppps/pdf/annex2.pdf

DIN 19739-1 (2002): Luftbeschaffenheit und Bodenbeschaffenheit - Messen der atmosphärischen Deposition organischer Spurenstoffe; Trichter-Adsorber-Verfahren - Teil 1: Sammelgeräte; Anforderungen, Aufbau, Anwendung. (Air and soil quality

- Measurement of atmospheric deposition of organic trace substances; Funnel adsorber method - Part 1: Sampling devices; Requirements, installation, application.) Beuth Verlag, Berlin.

DIN 38402-11 (2009): Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - Allgemeine Angaben (Gruppe A) - Teil 11: Probenahme von Abwasser (A 11). Beuth Verlag, Berlin.

DIN 38402-15 (2010): Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - Allgemeine Angaben (Gruppe A) - Teil 11: Probenahme aus Fließgewässern (A 15). Beuth Verlag, Berlin.

Dye, C., Schlabach, M., Green, J., Remberger, M., Kaj, L., Palm-Cousins, A., Brorström-Lundén, E. (2007): Bronopol, Resorcinol, m-Cresol and Triclosan in the Nordic Environment. Nordic Council of Ministers, Copenhagen, 2007.

EC (1998): Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market. Official Journal of the European Communities L 123/1-63, 24.4.98. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31998L0008&from=EN

EC (2000): Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal of the European Communities, L 327/1, 22.12.2000. http://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=PDF

EC (2008): Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. Official Journal of the European Union, L 348/84, 24.12.2008. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:348:0084:0097:EN:PDF

EC (2009a): Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status. Official Journal of the European Union, L 201/36, 1.8.2009. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:201:0036:0038:EN:PDF

EC (2009b): Guidance document No 19 - Guidance on surface water chemical monitoring under the Water Framework Directive. Common Implementation Strategy for the Water Framework Directive (2000/60/EC). Technical Report 2009 - 025. European Commission, Office for Official Publications of the European Communities, Luxembourg. https://circabc.europa.eu/sd/d/e54e8583-faf5-478f-9b11-41fda9e9c564/Guidance%20No%2019%20-%20Surface%20water%20chemical%20monitoring.pdf

EC (2010): Guidance document No 25 - Guidance on chemical monitoring of sediment and biota under the Water Framework Directive. Common Implementation Strategy for the Water Framework Directive (2000/60/EC). Technical Report 2010 - 041. European Commission, Office for Official Publications of the European Communities, Luxembourg. https://circabc.europa.eu/sd/d/7f47ccd9-ce47-4f4a-b4f0-cc61db518b1c/Guidance No 25 - Chemical Monitoring of Sediment and Biota.pdf

ECB (2008): Technical Guidance Document in support of the Directive 98/8/EC concerning the placing of biocidal products on the market, Guidance on data requirements for active substances and biocidal products, European Chemicals Bureau (ECB), Ispra, Italy, February 2008 (only editorial changes to the original version published in October 2000). http://ihcp.jrc.ec.europa.eu/our_activities/public-health/risk_assessment_of_Biocides/doc/TNsG/TNsG_DATA_REQUIREMENTS/TNsG-Data-Requirements.pdf

ECHA (2013): Guidance on information requirements. Guidance on regulation (EU) No 528/2012 concerning the making available on the market and use of biocidal products. Version 1.0. July 2013. European Chemicals Agency, Helsinki, Finnland. http://echa.europa.eu/documents/10162/15623299/biocides_guidance_information_requirements_en.pdf

Egli, H., Dassenakis, M., Garelick, H., van Grieken, R., Peijnenburg, W.J.G.M., Klasinc, L., Kördel, W., Priest, N., Tavares, T. (2003): Minimum requirements for reporting analytical data for environmental samples. Pure Appl. Chem. 75, 1097-1106.

EN ISO 11369 (1997): Water quality - Determination of selected plant treatment agents - Method using high performance liquid chromatography with UV detection after solid-liquid extraction (ISO 11369:1997). Beuth Verlag, Berlin, 1997.

EU (2012): Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products. Official Journal of the European Union, L 167/1, 27.6.2012. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:167:0001:0123:EN:PDF

EU (2013): Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union, L 226/1, 24.8.2013. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:226:0001:0017:EN:PDF

Fjeld, E., Schlabach, M., Berge, J.A., Eggen, T., Snilsberg, P., Källberg, G., Rognerud, S., Enge, E.K., Borgen, A., Gundersen, H. (2004): Kartlegging av utvalgte nye organiske miljøgifter -bromerte flammehemmere, klorerte parafiner, bisfenol A og triclosan (Screening of selected new organic contaminants - brominated flame retardants, chlorinated paraffins, bisphenol-A and triclosan; in Norwegian language with Englisch summary). Report TA2006, 2004. SFT, Oslo, Norway. http://www.miljodirektoratet.no/old/klif/publikasjoner/kjemikalier/2006/ta2006.pdf

Flores-Ramírez, R., Batres-Esquivel, L.E., Díaz-Barriga Martínez, F., López-Acosta, I., Ortiz-Pérez M.D. (2012): Development and validation of an analytical method to determine Fipronil and its degradation products in soil samples. Bull. Environ. Contam. Toxicol. 89, 744-750.

Fryer, R.J., Nicholson, M.D. (1999): Using smoothers for comprehensive assessment of contaminant time series in marine biota. ICES J. Mar. Sci. 56, 779-790.

Furdek, M., Vahcic, M., Scancar, J., Milacic, R., Kniewald, G., Mikac, N. (2012): Organotin compounds in seawater and Mytilus galloprovincialis mussels along the Croatian Adriatic Coast. Mar. Poll. Bull. 64, 189–199.

García-Valcárcel, A.I., Tadeo, J.L. (2011): Determination of azoles in sewage sludge from Spanish wastewater treatment plants by liquid chromatography-tandem mass spectrometry. J. Sep. Sci. 34, 1228-1235.

Gerrodette, T. (1993): Program TRENDS: User's Guide. Southwest Fisheries Science Center, P.O. Box 271, La Jolla, CA 92038. http://swfsc.noaa.gov/uploadedFiles/Divisions/PRD/Programs/ETP_Cetacean_Assessment/trends_guide.pdf

Gerrodette, T., Brandon, J. (2006): Trends. Version 3.0. Southwest Fisheries Science Center, La Jolla, California, USA. http://swfsc.noaa.gov/textblock.aspx?Division=PRD&ParentMenuId=228&id=4740

Giráldez, I., Chaguaceda, E., Bujalance, M., Morales, E. (2013): Determination of five booster biocides in seawater by stir bar sorptive extraction thermal desorption-gas chromatography-mass spectrometry. J. Chromatogr. A 1271, 17-26.

Gómez-Ramírez P, Shore RF, van den Brink NW, van Hattum B, Bustnes JO, Duke G, Fritsch C, García-Fernández AJ, Helander BO, Jaspers V, Krone O, Martínez-López E, Mateo R, Movalli P, Sonne C (2014): An overview of existing raptor contaminant monitoring activities in Europe. Environ. Int. 67C, 12-21.

Gustafson, D.I. (1989): Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environ. Toxicol. Chem. 8, 339-357.

Gustavsson, N., Bignert, A., Boalt, E., Nyberg, E., Stempa Tocca, J., Asplund, L., Eriksson, U., Nylund, K., Berger, U., Haglund P. (2010): Comments Concerning the National Swedish Contaminant Monitoring Programme in Freshwater Biota 2009. Report no. 4:2010. Swedish Museum of Natural History, Department of Contaminant Research, Stockholm, Sweden. http://www.nrm.se/download/18.42129f1312d951207af80001777/FCOM09.pdf

Hernández A.M., Bernal J., Bernal J.L., Martín M.T., Caminero C., Nozal M.J. (2013a): Simultaneous determination of nine anticoagulant rodenticides in soil and water by LC-ESI-MS. J. Sep. Sci. 36, 2593-2601.

Hernández A.M., Bernal J., Bernal J.L., Martín M.T., Caminero C., Nozal M.J. (2013b): Analysis of anticoagulant rodenticide residues in Microtus arvalis tissues by liquid chromatography with diode array, fluorescence and mass spectrometry detection. J. Chromatogr. (2013) 925 C, 76-85.

Hughes, J., Sharp, E., Taylor, M.J., Melton, L., Hartley, G. (2013): Monitoring agricultural rodenticide use and secondary exposure of raptors in Scotland. Ecotoxicology 22, 974-984

ISO 5667-1 (2006): Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1:2006); German version DIN EN ISO 5667-1 (2007): Wasserbeschaffenheit - Probenahme - Teil 1: Anleitung zur Erstellung von Probenahmeprogrammen und Probenahmetechniken. Beuth Verlag, Berlin

ISO 5667-3 (2012): Water quality - Sampling - Part 3: Preservation and handling of water samples. German version DIN EN ISO 5667-3 E (2013): Wasserbeschaffenheit - Probenahme - Teil 3: Konservierung und Handhabung von Wasserproben. Beuth Verlag, Berlin.

ISO 5667-11 (2009): Water quality - Sampling - Part 11: Guidance on sampling of groundwaters. Beuth Verlag, Berlin.

ISO 5667-13 (2011): Water quality - Sampling - Part 13: Guidance on sampling of sludges; German version EN ISO 5667-13 (2011):Wasserbeschaffenheit - Probenahme - Teil 13: Anleitung zur Probenahme von Schlämmen. Beuth Verlag, Berlin.

ISO 5667-14 (2013): Water quality. Sampling. Part 14. Guidance on quality assurance and quality control of environmental water sampling and handling. German version DIN ISO 5667-14 (2013): Wasserbeschaffenheit - Probenahme - Teil 14: Anleitung zur Qualitätssicherung bei der Entnahme und Handhabung von Wasserproben. Beuth Verlag, Berlin.

ISO 10381-1 (2002): Soil quality. Sampling. Part 1: Guidance on the design of sampling programmes. German version DIN ISO 10381-1 (2003): Bodenbeschaffenheit - Probenahme - Teil 1: Anleitung zur Aufstellung von Probenahmeprogrammen. Beuth Verlag, Berlin.

ISO 10381-2 (2002): Soil quality. Sampling. Part 2: Guidance on sampling techniques. German version DIN ISO 10381-2 (2003): Bodenbeschaffenheit - Probenahme - Teil 2: Anleitung für Probenahmeverfahren. Beuth Verlag, Berlin.

Jäger, S., Dulio, V., Schwarzbauer, J., Slobodnik, J., Rüdel, H. (2013): Environmental monitoring of biocides in Europe – from prioritisation to measurements. Workshop organised by NORMAN, Paris, and Umweltbundesamt, Dessau-Rosslau, November 5–6, 2012 in Berlin. Workshop Report, January 2013.

Jürgens, M.D., Johnson, A.C., Jones, K.C., Hughes, D., Lawlor, A.J. (2013): The presence of EU priority substances mercury, hexachlorobenzene, hexachlorobutadiene and PBDEs in wild fish from four English rivers. Sci. Total Environ. 461-462, 441-452.

Kahle, M., Nöh, I. (2009): Biozide in Gewässern - Eintragspfade und Informationen zur Belastungssituation und deren Auswirkungen. UBA-Texte 09/09, Umweltbundesamt, Dessau-Roßlau. http://opus.kobv.de/zlb/volltexte/2009/7730/pdf/3811.pdf

Karl, S., Thomas, K., Mayer, O., Schultze, B., Wilkinson, K., Scherzer, J., Trapp, M. (2013). GIS-gestützte Auswertung von PSM-Funden im Grundwasser im Rahmen von Monitoring und Fundaufklärungsverfahren: Entwicklung einer zusammenführenden Geodatenbank – Zeitliche und räumliche Analyse der Funddaten in Deutschland zur Identifizierung des Risikos für das Grundwasser am Beispiel des Wirkstoffs Bentazon sowie Ableitung von Bewertungsstrategien und Entscheidungskriterien. Report for project FKZ 360 03 052 by RLP Agroscience und UDATA, Neustadt/Weinstraße, for Umweltbundesamt, Dessau-Roßlau, June 2013.

Kördel, W., Garelick, H., Gawlik, B.M., Kandile, N.G., Peijnenburg, W.J., Rüdel, H. (2013): Substance-related environmental monitoring strategies regarding soil, groundwater and surface water - an overview. Environ. Sci. Pollut. Res. 20, 2810-2827.

Langford, K.H., Beylich, B.A., Bæk, K., Fjeld, E., Kringstad, A., Høyfeldt, A., Øxnevad, S., Thomas, K.V. (2012): Screening of selected alkylphenolic compounds, biocides, rodenticides and current use pesticides.

Langford, K.H., Reid, M., Thomas, K.V. (2013): The occurrence of second generation anticoagulant rodenticides in non-target raptor species in Norway. Sci. Total Environ. 450-451, 205-288.

LANUV (2014): PFT im Klärschlamm. Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen (LANUV). www.lanuv.nrw.de/abfall/pft_klaerschlamm.htm (accessed April 2014).

Law, R.J., Bolam, T., James, D., Barry, J., Deaville, R., Reid, R.J., Penrose, R., Jepson, P.D. (2012): Butyltin compounds in liver of harbour porpoises (Phocoena phocoena) from the UK prior to and following the ban on the use of tributyltin in antifouling paints (1992-2005 & 2009). Mar. Pollut. Bull. 64, 2576-2580.

LfU (2014): Bayerisches Landesamt für Umwelt (LfU). PFC-Belastungen in Abwasser und Klärschlamm. www.lfu.bayern.de/analytik_stoffe/analytik_org_stoffe_perfluorierte_chemikalien/pfc_belastung_abwasser_klaerschlamm/index.htm

Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R.H., Schwesig, D., Gawlik, B.M. (2013): EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Res. 47, 6475-6487.

LUBW (2014): Jahresdatenkatalog Fließgewässer 2011. Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (LUBW), Stuttgart, Germany. http://jdkfg.lubw.baden-wuerttemberg.de/servlet/is/300/

Luft, A., Wagner, M., Ternes, T.A. (2014): Transformation of biocides irgarol and terbutryn in the biological wastewater treatment. Environ. Sci. Technol. 48, 244-254.

Martínez-Carballo, E., Sitka, A., González-Barreiro, C., Kreuzinger, N., Fürhacker, M., Scharf, S., Gans, O. (2007a): Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part I. Application to surface, waste and indirect discharge water samples in Austria. Environ. Pollut. 145, 489-496.

Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Kreuzinger, N., Scharf, S., Gans, O. (2007b): Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II. Application to sediment and sludge samples in Austria. Environ. Pollut. 145, 543-547.

Morasch B., Bonvin F., Reiser H., Grandjean D., de Alencastro L.F., Perazzolo C., Chèvre N., Kohn T. (2010): Occurrence and fate of micropollutants in the Vidy Bay of Lake Geneva, Switzerland. Part II: micropollutant removal between wastewater and raw drinking water. Environ. Toxicol. Chem. 29, 1658-1668.

Nicholson, M.D., Fryer, R., Larsen, J.R. (1998): Temporal trend monitoring: robust method for analysing contaminant trend monitoring data. Techniques in Marine Environmental Sciences, No. 20. ICES, Copenhagen.

NLWKN (2009): Biota-Monitoring in niedersächsischen Gewässern – Untersuchung von Fischen auf Pflanzenschutzmittel, Oberirdische Gewässer, Band 30. Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz, Betriebsstelle Hannover-Hildesheim, 2009.

Nordic Council (2012): PPCP monitoring in the Nordic Countries – Status Report. TemaNord 2012:519, ISBN 9 78-92-893-2346-8. Nordic Council of Ministers, Copenhagen, 2012. http://www.norden.org/en/publications/publikationer/2012-519

Norström, K., Kaj, L., Brorström-Lundén, E. (2013): Screening 2012, Rodenticides. IVL report B2103. IVL Svenska Miljöinstitutet, Stockholm, Sweden, 2013. http://www.ivl.se/download/18.4dd97c213ed2e2e701ed7/1370939625747/B2103.pdf

OGewV (2011): Verordnung zum Schutz der Oberflächengewässer (Oberflächengewässerverordnung - OGewV) vom 20. Juli 2011. (German Surface Water Ordinance). Bundesgesetzblatt Jahrgang 2011 Teil I Nr. 37, 1429-1469. 25. Juli 2011. http://www.gesetze-im-internet.de/bundesrecht/ogewv/gesamt.pdf

Olofsson, U., Bignert, A., Haglund, P. (2012): Time-trends of metals and organic contaminants in sewage sludge. Water Res. 46, 4841-4851.

Ort, C., Lawrence, M.G., Reungoat, J., Mueller, J.F. (2010): Sampling for PPCPs in wastewater systems: comparison of different sampling modes and optimization strategies. Environ. Sci. Technol. 44, 6289-6296.

Palm Cousins, A., Brorström-Lundén, E., Hedlund, B. (2012): Prioritizing organic chemicals for long-term air monitoring by using empirical monitoring data--application to data from the Swedish screening program. Environ. Monit. Assess. 184, 4647-4654.

Plagellat, C., Kupper, T., de Alencastro, L.F., Grandjean, D., Tarradellas, J. (2004): Biocides in sewage sludge: quantitative determination in some Swiss wastewater treatment plants. Bull. Environ. Contam. Toxicol. 73, 794-801.

Remberger, M., Woldegiorgis, A., Kaj, L., Andersson J., Palm Cousins, A., Dusan, B., Ekhden, Y., Brorström-Lunden, E. (2006): Results from the Swedish Screening 2005, subreport 2. Biocides. IVL report B1700, November 2006. IVL Swedish Environmental Research Institute Ltd., Stockholm, Sweden. http://www.ivl.se/webdav/files/B-rapporter/B1700.pdf

Ruan, T., Song, S., Wang, T., Liu, R., Lin, Y., Jiang, G. (2014): Identification and Composition of Emerging Quaternary Ammonium Compounds in Municipal Sewage Sludge in China. Environ. Sci. Technol. 48, 4289-4297.

Rüdel, H., Fliedner, A. (2014): Umweltbelastung durch Biozide: Erarbeitung der Eckpfeiler eines Monitoring-Messprogrammes für Einträge von Bioziden in die Umwelt. Teilbericht zu AP III: Überprüfung, Überarbeitung und Vervollständigung des vorläufigen Priorisierungs-/Monitoring-Konzepts. Teilbericht des Fraunhofer IME, Schmallenberg, zu FKZ 3712 67 403 für das Umweltbundesamt, Dessau-Roßlau.

Rüdel, H., Knopf, B. (2012): Vorbereitung eines Monitoring-Konzepts für Biozide in der Umwelt, Abschlussbericht des Fraunhofer IME, Schmallenberg, zu FKZ 360 04 036 für das Umweltbundesamt, Dessau-Roßlau.

Rüdel, H., Weinfurtner, K. (2009): Überlegungen zur Umsetzung einer Klärschlammprobenahme im Rahmen der Umweltprobenbank des Bundes (in German language; includes a report of a workshop on sludge monitoring). Report by Fraunhofer-Institute for Molecular Biology and Applied Ecology, Schmallenberg, for Umweltbundesamt, Dessau-Roßlau. www.umweltprobenbank.de/en/documents/publications/12761

Rüdel, H., Steinhanses, J., Müller, J., Schröter-Kermani, C. (2009): Retrospektives Monitoring von Organozinnverbindungen in biologischen Proben aus Nord- und Ostsee - Sind die Anwendungsbeschränkungen erfolgreich? - BEITRAGSSERIE MEERESFORSCHUNG. Umweltwiss. Schadst. Forsch. 21, 282-291.

Rüdel, H., Weinfurtner, K., Koschorreck, J. (2010): Workshop of the German Environmental Specimen Bank on monitoring of priority pollutants and emerging substances in sewage sludge - Schmallenberg, Germany, June 24 to 25, 2009. Environ. Sci. Pollut. Res. 17, 1183-1185.

Rüdel, H., Müller, J., Quack, M., Klein, R. (2012): Monitoring of hexabromocyclododecane diastereomers in fish from European freshwaters and estuaries. Environ. Sci. Pollut. Res. 19, 772-783.

Rüdel, H., Böhmer, W., Müller, M., Fliedner, A., Ricking, M., Teubner, D., Schröter-Kermani, C. (2013): Retrospective study of triclosan and methyl-triclosan residues in fish and suspended particulate matter: results from the German Environmental Specimen Bank. Chemosphere 91, 1517-1524.

Salmi, T., Määttä, A., Anttila, P., Ruoho-Airola, T., Amnell, T. (2002): Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen's slope estimates - the EXCEL template application MAKESENS. Report code FMI-AQ-31. Finnish Meteorological Institute, Helsinki, Finland. http://en.ilmatieteenlaitos.fi/makesens

Sánchez-Barbudo, I.S., Camarero, P.R., Mateo, R. (2012): Primary and secondary poisoning by anticoagulant rodenticides of non-target animals in Spain. Sci. Total Environ. 420, 280-288.

SANCO (2010): Guidance document on pesticide residue analytical methods. Directorate General Health and Consumer Protection, European Commission. Document No. SANCO/825/00 rev. 8.1, 6 16/11/2010. http://ec.europa.eu/food/plant/protection/resources/guide_doc_825-00_rev7_en.pdf

SANCO (2011): Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed. Directorate General Health and Consumer Protection, European Commission. Document No. SANCO/12495/2011. http://ec.europa.eu/food/plant/plant_protection_products/guidance_documents/docs/qualcontrol_en.pdf

Schubert, B., Heininger, P., Keller, M., Ricking, M., Claus, E. (2012): Monitoring of contaminants in suspended particulate matter as an alternative to sediments. Trends Anal. Chem. 36, 58–70.

Schulz, V. (2013): Zeitreihenuntersuchung von Irgarol und den Azolfungiziden Tebuconazol und Propiconazol in Schwebstoffproben der Umweltprobenbank des Bundes (UPB). Abschlussbericht der FOOD GmbH Jena Analytik-Consulting zu Projektnummer 28 221 für das Umweltbundesamt Dessau-Roßlau. http://www.umweltprobenbank.de/upb_static/fck/download/Abschlussbericht%20%2013-12-20_kb.pdf

Subedi, B., Du, B., Chambliss, C.K., Koschorreck, J., Rüdel, H., Quack, M., Brooks, B.W., Usenko, S. (2012): Occurrence of pharmaceuticals and personal care products in German fish tissue: a national study. Environ. Sci. Technol. 46, 9047-9054.

TNsG (2009): TNsG on Data Requirements, Part A, Chapter 2, Point 4 "Analytical Methods for Detection and Identification" and Part B, Chapter 2, Point 4 "Methods of Identification and Analysis". Technical Notes for Guidance (TNsG) were adopted during the 33rd meeting of representatives of Members States Competent Authorities for the implementation of Directive 98/8/EC concerning the placing of biocidal products on the market, 13-15 May 2009.

Tosh D.G., McDonald R.A., Bearhop S., Llewellyn N.R., Montgomery W.I., Shore R.F. (2012): Rodenticide exposure in wood mouse and house mouse populations on farms and potential secondary risk to predators. Ecotoxicology 21, 1325-1232.

TZW (2012): Studie zur Bedeutung von Bioziden für die Trinkwasserversorgung. Research report (in German language). Band 53, ISSN 1434-5765. Technologiezentrum Wasser (TZW), Karlsruhe, Germany, June 2012.

UBA (2013): LOESS-Trend. Version 1.0 (August 2013). Microsoft Excel-based tool. J. Wellmitz, Labor für Wasseranalytik, Umweltbundesamt, Berlin.

VDI 4230-2 (2008): Biological procedures to determine effects of air pollutants (bioindication) - Biomonitoring with earthworms. German Version: Biologische Verfahren zur Erfassung der Wirkung von Luftverunreinigungen (Bioindikation) - Passives Biomonitoring mit Regenwürmern als Akkumulationsindikatoren. Beuth Verlag, Berlin.

Vermeirssen, E.L.M., Bramaz, N., Hollender, J., Singer, H., Escher B.I. (2009): Passive sampling combined with ecotoxicological and chemical analysis of pharmaceuticals and biocides - evaluation of three ChemcatcherTM configurations. Water Res. 43, 903-914.

von der Ohe, P.C., Schmitt-Jansen, M., Slobodnik, J., Brack, W. (2012). Triclosan--the forgotten priority substance? Environ. Sci. Pollut. Res. 19, 585-591.

von der Trenck, K.T. (2012). Warndienst Wanderfalke - Vogeleier spiegeln langlebige Umwelt-Gifte. Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (LUBW), Stuttgart, Germany. http://www.fachdokumente.lubw.baden-wuerttemberg.de/servlet/is/101766/U52-M341-N11.pdf?command=downloadContent&filename=U52-M341-N11.pdf&FIS=91063

Vorkamp K., Bossi R., Bester K., Bollmann U.E., Boutrup S. (2014): New priority substances of the European Water Framework Directive: biocides, pesticides and brominated flame retardants in the aquatic environment of Denmark. Sci. Total Environ. 470-471, 459-468.

Vrana, B., Vermeirssen, E.L.M., Allan, I.J., Kohoutek, J., Kennedy K., Mills, G.A., Greenwood, R. (2010): Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives. Position paper. NORMAN Association, Paris, France. http://www.norman-network.net/sites/default/files/norman_position_paper_pas_sampling.pdf

Walker, L.A., Llewellyn, N.R., Pereira, M.G., Potter, E.D., Sainsbury, A.W., Shore, R.F. (2012): Anticoagulant rodenticides in predatory birds 2010: a Predatory Bird Monitoring Scheme (PBMS) report. Centre for Ecology & Hydrology, Lancaster, UK. http://nora.nerc.ac.uk/20220/

Walker, L.A., Turk, A., Long, S.M., Wienburg, C.L., Best, J., Shore, R.F. (2008): Second generation anticoagulant rodenticides in tawny owls (Strix aluco) from Great Britain. Sci. Total Environ. 392, 93-98.

Wick, A., Fink, G., Ternes, T. A. (2010): Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1217, 2088-2103.

Wittmer, I. K., Scheidegger, R., Bader, H. P., Singer, H., Stamm, C. (2011): Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409, 920-932.

Woldegiorgis, A., Remberger, M., Kaj, L., Green, J., Ekheden, Y., Palm Cousins, A., Brorström-Lundén, E., Dye, C., Aspmo, K., Vadset, M., Schlabach, M., Langford, K. (2007): Results from the Swedish Screening Programme 2006 - Subreport 3: Zinc pyrithione and Irgarol 1051. Report B1764. IVL Swedish Environmental Research Institute Ltd., Stockholm, Sweden. www.ivl.se/download/18.7df4c4e812d2da6a416800071959/B1764.pdf

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Evaluation of monitoring data and application for the validation of the proposed concepts for the prioritisation and monitoring of biocides (Annex 7)

Teilbericht zum Projekt: Umweltbelastung durch Biozide: Erarbeitung der Eckpfeiler eines Monitoring-Messprogrammes für Einträge von Bioziden in die Umwelt

by

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Kurzbeschreibung

Biozidmonitoring-Daten aus verschiedenen Quellen wurden recherchiert und in Bezug auf die untersuchten Wirkstoffe, den Anteil an Proben mit einem Gehalt über der jeweiligen analytischen Bestimmungsgrenze (BG), und dem Anteil an Proben mit Konzentrationen über den Effektschwellen (predicted no effect concentrations, PNECs, oder Umweltqualitätsnormen, UQNs) ausgewertet. Die meisten recherchierten Daten stammen aus dem Oberflächengewässermonitoring (Wasserphase, teilweise Biota oder Schwebstoffe). Die wichtigsten ausgewerteten Datensätze sind: ein größerer Satz Gewässermonitoring-Daten für etwa 20 Biozide, der vom bayerischen LfU bereitgestellt wurde; aggregierte Datensätze (Fact Sheets) für etwa 10 Biozidwirkstoffe mit Monitoring-Daten aus mehreren europäischen Ländern aus der EMPODAT Datenbank des NORMAN-Netzwerks (hauptsächlich Wasser); Datensätze aus der Flusswassermonitoring-Datenbank der europäischen Umweltagentur (EEA); Schwebstoffmonitoring-Daten für mehrere Biozide aus retrospektiven Analysen von archivierten Proben aus der Umweltprobenbank des Bundes. Die Wasserkonzentrationen lagen für eine Mehrzahl der betrachteten Biozide unterhalb der jeweiligen BG. Für einige Verbindungen wurden aber auch Überschreitungen der Wirkschwellen beobachtet. Für bestimmte Biozide war die angewandte BG zu hoch (größer als die PNEC/UQN), so dass keine Überprüfung von Schwellenwertüberschreitungen möglich war. Wenn die recherchierten Datensätze Zeitreihen enthielten, wurden diese hinsichtlich möglicher Trends ausgewertet, beispielsweise um zu prüfen, ob Änderungen der Umweltkonzentrationen mit Genehmigungsentscheidungen für diese Biozide korrelieren. Schließlich wurden die verfügbaren Monitoring-Daten für die Validierung eines zuvor entwickelten Priorisierungskonzepts für Biozide genutzt. Die Priorisierung erfolgt in Bezug auf die Relevanz des Auftretens eines Stoffes in der Umwelt und die möglicherweise durch den Stoff verursachten unerwünschten Wirkungen. Dabei wurde insbesondere geprüft, ob die Monitoring-Daten die Anwesenheit der priorisierten Verbindungen in den entsprechenden im Priorisierungsschema identifizierten Kompartimenten bestätigen.

Abstract

Biocides monitoring data from several sources were retrieved and evaluated regarding the covered compounds, the fraction of samples with levels above the respective analytical limit of quantification (LOQ), and the fraction of samples with concentrations exceeding effect levels (predicted no effect concentrations, PNECs, or environmental quality standards, EQSs). Retrieved data were mainly from surface water monitoring (water phase, partly biota or suspended particulate matter, SPM). The main data sets evaluated were: a larger surface water data set with biocides monitoring data for about 20 compounds kindly provided by the Bavarian Environment Agency (LfU); aggregated data sets (fact sheets) for about 10 biocidal compounds with relevant monitoring data from several European countries retrieved from the EMPODAT data base of the NORMAN association (mainly water); data sets from the European Environment Agency (EEA) river water monitoring data base; SPM monitoring data for several biocides from retrospective analysis of archived samples from the German Environmental Specimen Bank. The water phase concentrations for most of the biocides were below the respective LOQ. However, for some compounds also the exceedance of effect thresholds were observed. For certain biocides the applied LOQ was too high (above the PNEC/EQS) to allow checking of exceedance of effect levels. If the retrieved data sets contained time series these were evaluated for possible trends, e.g., to prove whether changes in environmental concentrations were correlated with approval decisions for these biocides. Finally, the available monitoring data were applied for the validation of a previously developed prioritisation concept for biocides. The prioritisation is based on the relevance of a chemical for occurring in the environment and causing adverse effects. It was especially assessed whether the monitoring data are confirming the presence of prioritised compounds in the respective compartments identified in the prioritisation approach.

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AA	annual average
BPR	Biocidal Products Regulation No. 528/2012
DEET	N,N-diethyltoluamide
dw	dry weight
EEA	European Environment Agency
ESB	Environmental Specimen Bank
EQS	environmental quality standard
EU	European Union
K_{OC}	partition coefficient organic carbon/water
LfU	Bayerisches Landesamt für Umwelt (Bavarian Environmental Agency)
LOQ	limit of quantification
PNEC	predicted no effect concentration
PPP	plant protection product
PT	product type
QSAR	quantitative structure-activity relationship
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation (EC) No 1907/2006)
STP	sewage treatment plant
WFD	Water Framework Directive

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The authors acknowledge the kindly provision of monitoring data by the Bavarian Environmental Agency (Bayerisches Landesamt für Umwelt, LfU). We thank the NORMAN network for sharing the biocides monitoring data from the EMPODAT database.

1 Aim of the study

To get an overview on available biocides monitoring data a literature search was conducted as part of the project (refer to section "Literature compilation on biocides monitoring" in Rüdel et al. 2015, main report). Beside publications, also online databases covering biocides monitoring data were identified and data sets retrieved, if possible. The compiled biocides monitoring data sets were evaluated regarding the covered compounds, the fraction of samples with levels above the respective limit of quantification (LOQ), and the fraction of samples with concentrations exceeding effect levels (for example, predicted no effect concentrations, PNECs, or environmental quality standards, EQSs). Finally, the available monitoring data should be applied for the validation of a previously developed prioritisation concept for biocides (Rüdel and Fliedner 2014a, Annex 2). The prioritisation is based on the relevance of a chemical for occurring in the environment and causing adverse effects. It was assessed whether the monitoring data are confirming the presence of prioritised compounds in the respective compartments identified in the prioritisation approach.

2 Evaluation of biocides monitoring data sets

2.1 Data from the Bavarian Environment Agency (LfU)

A larger data set with biocides monitoring data (surface water) was provided by the Bavarian Environment Agency (LfU). Samples were collected for the routine Water Framework Directive (WFD) monitoring but analysed for additional compounds beside obligatory priority compounds. Samplings were performed at a large number of sites in Bavaria in the period 2010-2013 (in some cases repeated samplings were performed). The data cover 20 compounds which have different approval status as biocides. The data were formatted in the Excel-based data collection template developed by the NORMAN association (www.norman-network.net/empodat/dct_download_index.php). The data contain information on the sampling sites (incl. geo-coordinates), dates, compounds and concentrations (if above the limit of quantification, LOQ). An example data set is shown in Figure 1. In a separate sheet the LOQ and other method-related information are provided.

Figure 1: Excerpt from the LfU biocides monitoring data set provided in the Excel-based NORMAN data collection template.

SAMPLING SITE / STATION			ECOSYSTEM / MATRIX: WATER	DETERMINAND / MEASURAND	INDIVIDUAL CONCENTRATION				
Station name and codes	Longitude	Latitude	Sample matrix	Individual compound	Concentration	Value	Unit		
Name	Decimal	Decimal						Month	Year
oh.Mdg. - Br. "Am Bach"	12.370498	48.957591	Surface water - River water	terbuthylazine	Individual Value	0.36	µg/l	6	2010
Bauhof Zirndorf	10.969259	49.439714	Surface water - River water	terbuthylazine	Individual Value	0.01	µg/l	11	2011
SEEMUEHLE BRUECKE	11.985035	48.679056	Surface water - River water	terbuthylazine	Individual Value	0.01	µg/l	11	2011
Grafenmuehle UW	13.143556	48.610158	Surface water - River water	terbuthylazine	Individual Value	0.03	µg/l	12	2011
Grafenmuehle UW	13.143556	48.610158	Surface water - River water	Chlorotoluron	Individual Value	0.04	µg/l	12	2011
Ruhstorf Pegel	13.333977	48.428287	Surface water - River water	terbuthylazine	Individual Value	0.02	µg/l	12	2011
Jochenstein Messstation	13.702132	48.520707	Surface water - River water	Irgarol	Individual Value	0.0031	µg/l	3	2012
oh.Mdg. - Br. "Am Bach"	12.370498	48.957591	Surface water - River water	terbuthylazine	Individual Value	0.31	µg/l	5	2012
oh.Mdg. - Br. "Am Bach"	12.370498	48.957591	Surface water - River water	Propiconazole	Individual Value	0.02	µg/l	5	2012
Schönach Pegel	12.423665	48.915082	Surface water - River water	terbuthylazine	Individual Value	0.12	µg/l	5	2012
Bauhof Zirndorf	10.969259	49.439714	Surface water - River water	terbuthylazine	Individual Value	0.08	µg/l	5	2012
Grafenmuehle UW	13.143556	48.610158	Surface water - River water	terbuthylazine	Individual Value	0.04	µg/l	8	2012
Ruhstorf Pegel	13.333977	48.428287	Surface water - River water	terbuthylazine	Individual Value	0.03	µg/l	8	2012
Egermühle, Steg	10.627665	48.810326	Surface water - River water	Carbendazim	Individual Value	0.05	µg/l	9	2012
Schulmühle,vor Mdg. in die Leinleiter	11.194330	49.845859	Surface water - River water	terbuthylazine	Individual Value	0.03	µg/l	6	2013
Schulmühle,vor Mdg. in die Leinleiter	11.194330	49.845859	Surface water - River water	Chlorotoluron	Individual Value	0.03	µg/l	6	2013
Egermühle, Steg	10.627665	48.810326	Surface water - River water	terbuthylazine	Individual Value	0.07	µg/l	6	2013
oh.Mdg. - Br. "Am Bach"	12.370498	48.957591	Surface water - River water	terbuthylazine	Individual Value	0.02	µg/l	10	2013
Bauhof Zirndorf	10.969259	49.439714	Surface water - River water	terbuthylazine	Individual Value	0.01	µg/l	10	2013
Grafenmuehle UW	13.143556	48.610158	Surface water - River water	terbuthylazine	Individual Value	0.01	µg/l	10	2010
Ruhstorf Pegel	13.333977	48.428287	Surface water - River water	terbuthylazine	Individual Value	0.02	µg/l	10	2010
Egermühle, Steg	10.627665	48.810326	Surface water - River water	terbuthylazine	Individual Value	0.16	µg/l	7	2011
o.KA Meeder	10.926122	50.297547	Surface water - River water	terbuthylazine	Individual Value	0.04	µg/l	7	2011
Schulmühle,vor Mdg. in die Leinleiter	11.194330	49.845859	Surface water - River water	terbuthylazine	Individual Value	0.06	µg/l	7	2011
Bauhof Zirndorf	10.969259	49.439714	Surface water - River water	terbuthylazine	Individual Value	0.03	µg/l	8	2011
SEEMUEHLE BRUECKE	11.985035	48.679056	Surface water - River water	Chlorotoluron	Individual Value	0.08	µg/l	9	2011
SEEMUEHLE BRUECKE	11.985035	48.679056	Surface water - River water	terbuthylazine	Individual Value	0.18	µg/l	9	2011

Some compounds in the LfU compilation are (or were) not only approved as biocides in the EU but also as plant protection products (PPP) or under other regulations (e.g. as pharmaceuticals or industrial chemicals). Some compounds are no longer approved at all (e.g., malathion or prometryn). Compounds currently approved as biocides, but not as PPP, are diuron, tolylfluanid and permethrin (also used as a pharmaceutical). Recently, non-approval decisions were published for the active substances cybutryne (Irgarol) and triclosan. These substances have to be phase out in biocidal products one year after publication at the latest (products no longer allowed on the market after January 2017).

The data set is characterised in Table 1. In some cases the limits of quantification (LOQs) seem not to be appropriate since the PNEC values are lower than the LOQs. For the WFD monitoring it is required to achieve a LOQ of 30 % of the EQS of the target compound (according to Directive 2009/90/EC on the technical specifications for chemical analysis and monitoring of water status; EC 2009).

Table 1: Description of the data set provided in March 2015 by the Bavarian Environment Agency (LfU). red: LOQ › PNEC; green: compound currently only used as biocide.

Analyte	no. of data sets	no. of data above LOQ	approval status (May 2015)	LOQ min [µg/L]	LOQ max [µg/L]	PNEC [µg/L][1]	AA EQS [µg/L][2]
Carbendazim	1205	43	biocide, PPP until 30.11.2014	0.02	0.05	-	-
Chlorotoluron	1205	81	PPP, former biocide	0.01	0.05	-	0.4
Cyfluthrin	522	0	biocide, PPP		0.05	0.001	
Cypermethrin	520	0	biocide, PPP		0.025	0.001	0.00008
Cyproconazole	528	1	biocide, PPP	0.01	0.05	2.1	-
Diazinon	591	3	former biocide, former PPP	0.005	0.05	-	0.01
Dimethoate	530	4	PPP, former biocide	0.01	0.05	-	0.1
Diuron	1239	38	biocide, former PPP	0.01	0.05	-	0.2
Fenpropimorph	528	1	biocide, PPP	0.02	0.05	0.016	-
Imidacloprid	1205	15	biocide, PPP	0.02	0.05	0.174	-
Cybutryne (Irgarol)	266	28	biocide[3]	0.0004	0.01	0.0058	0.0025
Isoproturon	1239	437	biocide, PPP	0.02	0.05	-	0.3
Malathion	449	0	former biocide		0.02	-	0.02
Permethrin	521	0	biocide		0.005	0.000094	-
Prometryn	530	0	former biocide	0.01	0.05	-	0.5
Propiconazole	1205	43	biocide, PPP	0.02	0.05	6.8	1
Tebuconazole	1238	57	biocide, PPP	0.02	0.05	1.0	-

Analyte	no. of data sets	no. of data above LOQ	approval status (May 2015)	LOQ min [µg/L]	LOQ max [µg/L]	PNEC [µg/L][1]	AA EQS [µg/L][2]
Terbuthylazine	1205	432	PPP, former biocide	0.01	0.05	-	0.5
Tolylfluanid	54	0	biocide, former PPP		0.03	0.265	-
Triclosan	14	12	biocide[4]		0.001	0.05	-
Total no.:	14794	1195					

[1]: PNEC - predicted no effect concentration according to the respective EU biocide assessment report;
[2]: AA-EQS - annual average environmental quality standard (according to Directive 2013/39/EU, specifying the Water Framework Directive).
[3] Recently a non-approval decision was published for cybutryne (Irgarol) for PT 21; the substance has to be phased out in biocidal products one year after publication at the latest (products no longer allowed on the market after January 2017).
[4] Recently a non-approval decision was published for triclosan for PT 1; the substance has to be phased out in biocidal products one year after publication at the latest (products no longer allowed on the market after January 2017).
PPP -plant protection product. LOQ - limit of quantification.

Overall, only in about 10 % of the analyses compounds were detected above the respective LOQ. However, in some cases the achieved LOQ are above the predicted PNEC according to the respective EU biocide assessment report or the annual average environmental quality standard (AA-EQS) according to Directive 2013/39/EU (EQS-Directive, specifying the WFD; EU 2013), e.g., cyfluthrin, cypermethrin or permethrin. For these compounds an exceedance of the threshold would not be identified by the analyses.

For some compounds monitoring data were examined in detail.

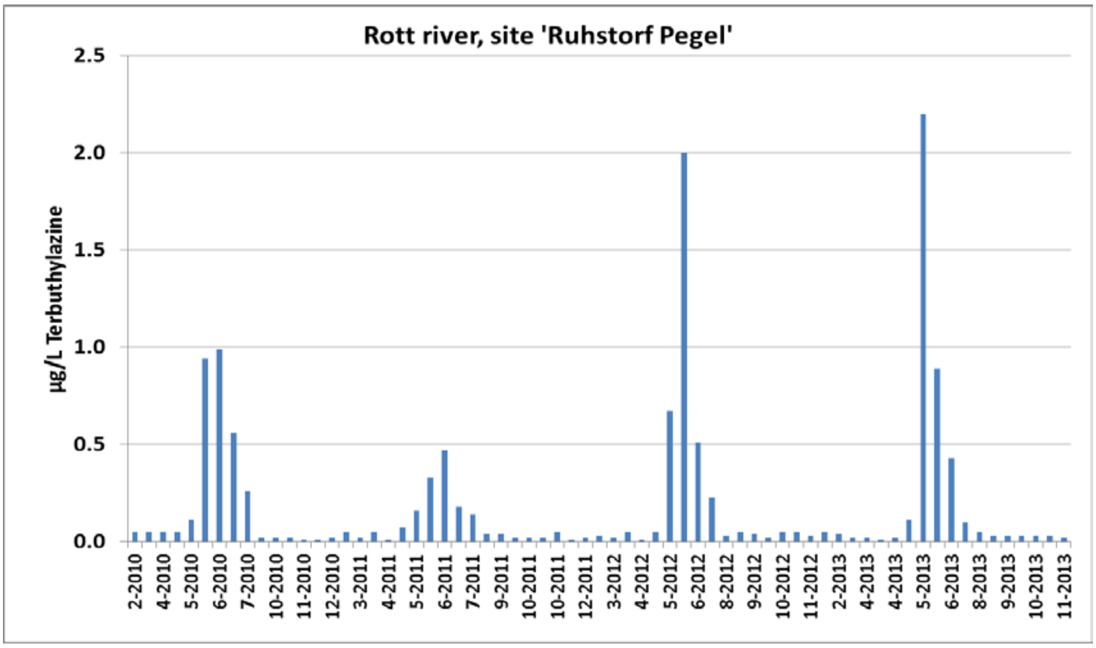
For cybutryne (Irgarol), values above the LOQ were especially detected at the Main river site ‘Kahl a. Main, Messstation (SH Krotzenburg, km 067.1)’. At this site eight of ten data were above the LOQ in 2010. However, in the whole data set only one value exceeded the EQS (0.0031 µg/L, Danube, site Jochenstein, March 2012).

For isoproturon about 35% of the approx. 1240 data sets were above the LOQ. However, most of them were below the respective EQS. Only six values exceeded the EQS (maximum value 1.2 µg/L). The water bodies with exceedances were Main, Sulzbach, and Grosse Laber. In the period 2010 - 2013 exceedances were observed especially in autumn/winter months.

Terbuthylazine (36 % of approx. 1200 data sets above LOQ) showed some exceedances of the EQS. Periods of high concentrations in water were the months May to July in the years 2010 - 2013 (e.g. at the site Ruhstorf Pegel of the river Rott, see Figure 2). In these periods the EQS was also partly exceeded (the same holds true for other sites). The seasonal findings support that the inputs are probably caused by agricultural usage of the compound (in the EU the usage as biocide was phased-out in February 2011).

Tebuconazole concentrations above the LOQ were often found in the small river Grosse Laber (e.g., sites ‘Schönach Pegel’ and ‘Seemuehle Bruecke’). These findings were observed in the months April to November in the years 2010 - 2013 and are assumed to have primarily an agricultural origin.

Figure 2: Data from the surface water monitoring of terbuthylazine in the river Rott near Ruhstorf; values below the LOQ were substituted by a value of 50% of the LOQ. Data (as µg/L) were provided by LfU. Dates are given as month-year.



For triclosan only few data was available. However, of the 14 data measured at several sites in the year 2010, 12 were above the LOQ (0.001 µg/L). Data were in the range 0.001 - 0.013 µg/L. Thus the PNEC according to the respective EU biocide assessment report (0.05 µg/L) and the PNEC applied for the EU REACH assessment (0.07 µg/L)[1] were not exceeded. However, in a study by von der Ohe et al. (2012) a lower PNEC for triclosan was derived (0.0047 µg/L). If this PNEC is applied it would have been exceeded in two cases (at two dates at the site "Hausen, Messstation"). For the Elbe river basin, von der Ohe et al. (2012) reported exceedances of the PNEC of 0.0047 µg/L at 75% of the sites for the period 2006 - 2008.

2.2 Data from the NORMAN data base EMPODAT

The NORMAN association operates a huge data base with monitoring data from monitoring programmes of EU member states, from integrated projects as well as from member institutions. At present France and Germany (mostly from the federal state of Saxony) are by far the main data contributors to EMPODAT, followed by The Netherlands and Slovakia. Beside the analytical data also information on the sampling sites (incl. geo-coordinates) and dates are recorded. The data base covers different matrices (mostly from the aquatic environment). Partly also quality assurance-related information is provided with the original data sets.

The NORMAN EMPODAT database was exemplarily evaluated for a set of biocides. A focus was directed on those biocides which are currently not approved as PPPs. Another prerequisite was that larger data sets with data above the LOQ were available in the EMPODAT database. For these compounds it was also checked whether exceedances of PNEC values were observed. Examples are triclosan, N,N-diethyltoluamide (DEET), dichlofluanid, permethrin, terbutryn, cyfluthrin, and cybutryne (Irgarol) which are discussed below.

[1] Source: ECHA data on triclosan, retrieved at http://bit.ly/1PbOUOl (accessed October 2015).

Table 2 gives an overview over the monitoring data for triclosan available in EMPODAT. By far the most data are available for river water (80 % above the LOQ). The median concentration of 0.013 µg/L is in the range of the lowest aquatic PNEC derived by NORMAN of 0.02 µg/L (similar to the EQS proposal derived in Germany; Wenzel et al. 2015), but is below the PNEC derived during the assessment of triclosan as biocide (0.05 µg/L). Concentrations of triclosan in sediments from lakes and rivers, on the other hand, are exceeding the respective PNEC for this matrix (calculated from the aquatic PNEC by applying the equilibrium-partitioning method). The same holds true for the respective PNEC for lake fish samples. However, there is only a slight exceedance and the database for this matrix is quite low (only 8 data sets from Germany and Sweden; partly from sites downstream of STPs). Moreover, the fact sheet gives information on the origin of the data and the covered period (e.g.: France - 289 stations, 1435 data, period 2011 - 2012; Germany - 682 stations, 12609 data, mainly from the period 2006 - 2012; Italy - 45 stations, 50 data, period 2006 - 2007).

Table 2: NORMAN EMPODAT fact sheet on triclosan (status October 2015).

Matrix	Total no. of analyses	No. of analysis above LOQ	Maximum value	Median	Unit	Lowest PNEC[1]	EQS
Biota - Lake water	8	3	52	4.1	µg/kg wet weight	3.04	n.a.
Biota - River water	90	35	31	0.49	µg/kg wet weight	3.04	n.a.
Sediments - Lake water	22	4	290	36.5	µg/kg dry weight	7.65	n.a.
Sediments - River water	112	5	65	28.7	µg/kg dry weight	7.65	n.a.
Sewage sludge - Industrial	1	1	1200	1200	µg/kg dry weight	n.a.	n.a.
Sewage sludge -Municipal	8	8	3800	1700	µg/kg dry weight	n.a.	n.a.
Sewage sludge - Other	6	6	4800	3350	µg/kg dry weight	n.a.	n.a.
Suspended matter - other	1	1	1410	1410	µg/kg dry weight	n.a.	n.a.
Water - Ground water	953	-	-	-	µg/L	0.02	n.a.
Water - Surface water- Lake water	186	133	0.18	0.007	µg/L	0.02	n.a.
Water - Surface water- River water	12888	10342	3.06	0.013	µg/L	0.02	n.a.

Matrix	Total no. of analyses	No. of analysis above LOQ	Maxi-mum value	Median	Unit	Lowest PNEC[1]	EQS
Water - Waste water - Industrial	6	6	0.046	0.04	µg/L	0.02	n.a.
Water - Waste water - Municipal	12	12	0.013	0.705	µg/L	0.02	n.a.
Water - Waste water -Other	1	1	0.0052	0.0052	µg/L	0.02	n.a.

[1]: Lowest PNEC - lowest predicted no effect concentration according to the NORMAN data base (re-calculated for the different matrices);
[2]: EQS - environmental quality standard according to WFD (no WFD EQS implemented for triclosan).
n.a. - not available. LOQ - limit of quantification.

For cybutryne (Irgarol) about 8400 surface water data sets are available for river water in the NORMAN EMPODAT database. About 40 % of the data are reported to be above the LOQ. The median concentration of cybutryne in rivers is 0.005 µg/L. This concentration value is in the range of the PNEC of 0.0058 µg/L derived for cybutryne in the EU biocide assessment report and twice the annual average EQS of 0.0025 µg/L set in the EQS-Directive 2013/39/EU (EU 2013) for cybutryne (Table 3).

Another compound selected for evaluation was N,N-diethyltoluamide (DEET). For this compound EMPODAT data are mainly available for Germany. DEET was frequently detected in surface waters but no exceedances of the PNEC were observed (Table 3). Only in one lake water sample from Sweden a clear exceedance was observed (1100 µg/L). However, it may be that this high concentration results from a transmission error since this value is at least 1000 times higher than the DEET concentration measured for other Swedish lakes.

For dichlofluanid data from three countries are available in EMPODAT. Most data (about 90 %) are from France, about 10 % from The Netherlands and only a small number from Sweden. The detected median concentrations of dichlofluanid in lake water exceed the PNEC applied by NORMAN (0.01 µg/L) by a factor of 2 while the concentration in river water equals the PNEC level. The PNEC of dichlofluanid derived from the ecotoxicity data in the EU biocide assessment report is higher (Table 3) and is not exceeded by the measured concentrations.

For permethrin, mainly data from France are available in EMPODAT. The median concentration in river water is 0.05 µg/L which is about 20 times the PNEC of 0.0023 µg/L applied by NORMAN. However, the median is about 500 times higher than the PNEC of permethrin derived from the ecotoxicity data in the EU biocide assessment report (Table 3). The situation for cyfluthrin is similar. Again, the NORMAN PNEC for cyfluthrin of 0.005 µg/L is clearly exceeded by the median concentration of 0.1 µg/L in river water (factor of 20). For terbutryn, too, frequent exceedances of the PNEC of 0.0024 µg/L applied by NORMAN are observed. The median concentrations for river as well as lake water are higher than the PNEC (Table 3).

For the latter compounds it has to be considered additionally that the applied LOQ are often not sensitive enough to test the compliance at the effect levels. Thus, with a more sensitive method further exceedances may be detected in the fraction of 80 - 90 % of the data with concentrations below the currently achieved LOQs.

NORMAN fact sheets for further biocides are provided in a separate pdf-file. A summary of the relevant surface water data is provided in Table 3.

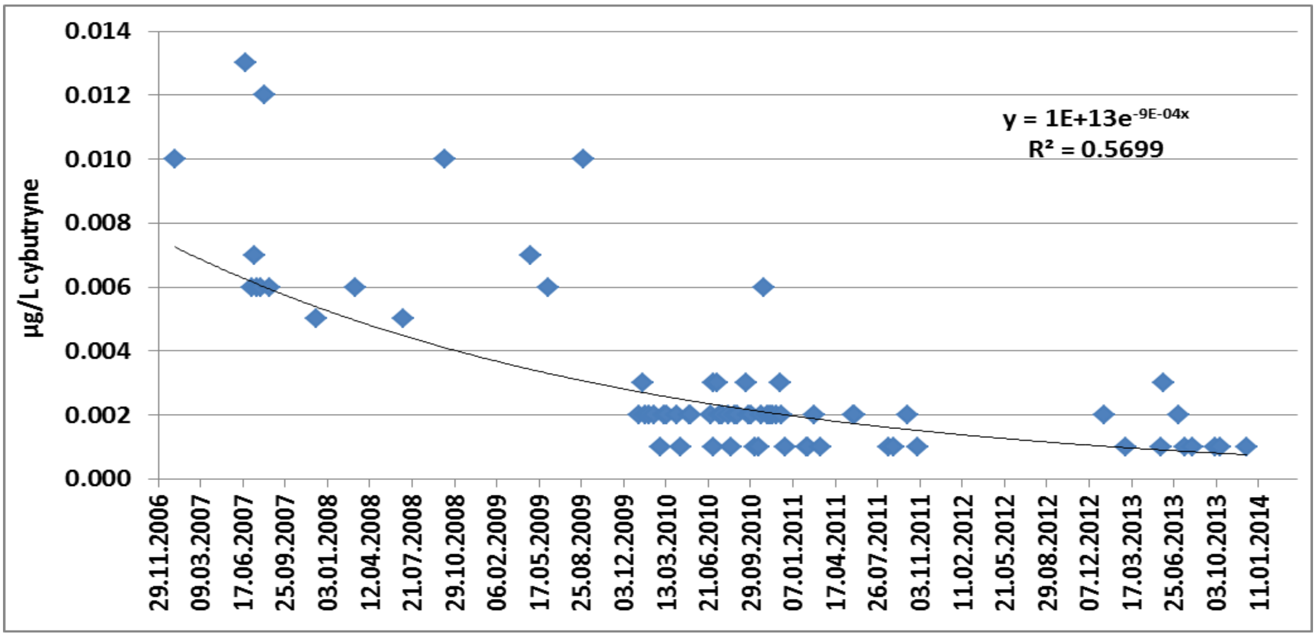
Table 3: Evaluation of NORMAN EMPODAT fact sheets on biocides which are not approved as plant protection products (status October 2015).

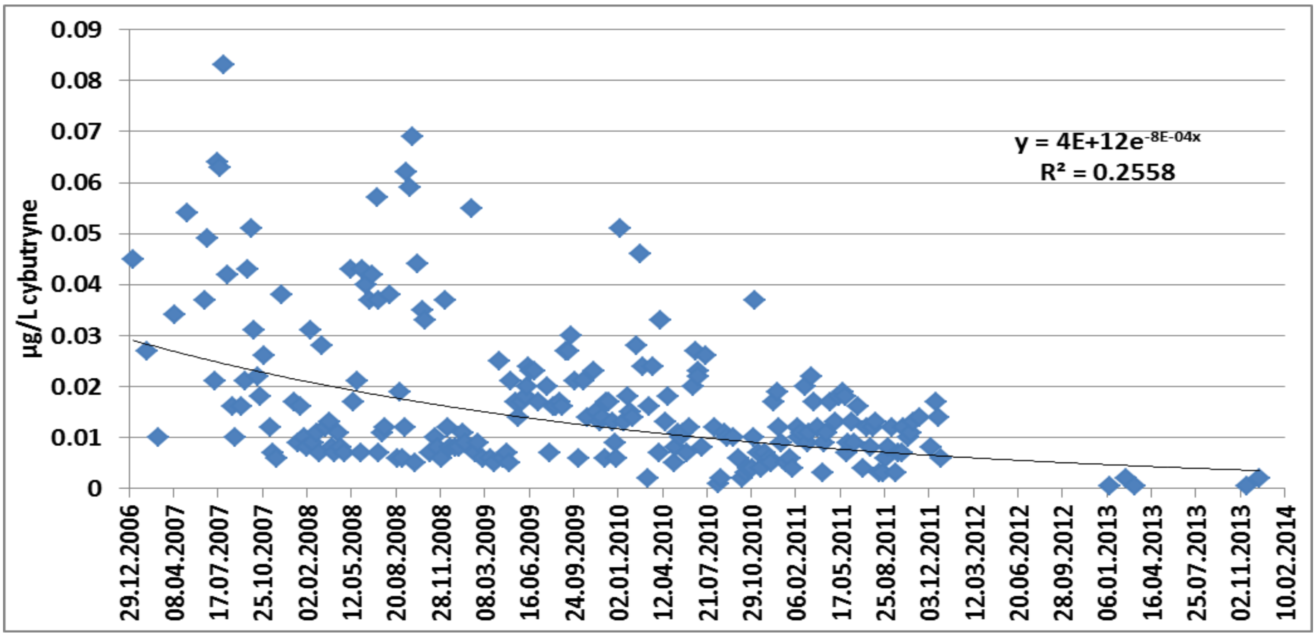
Biocide name	CAS no.	PNEC NORMAN	PNEC EU report ¥	Median lakes µg/L	Median rivers µg/L	% of data above LOQ lake/river	Data no. above LOQ lake/river
o-Benzyl-p-chlorophenol (Clorophene)	120-32-1	0.59	-	-	0.125	- / 12	- / 90
Cybutryne (Irgarol)	28159-98-0	0.0025^Δ	0.0058	0.002	0.005	39 /39	27 / 3258
Cyfluthrin	68359-37-5	0.005	0.001	-	0.1	- / 12	- / 4748
N,N-Diethylto-luamide (DEET)	134-62-3	41	43	0.005	0.012	93 / 85	331 / 12882
Dichlofluanid&	1085-98-9	0.01	0.053	0.02	0.01	3 / 6	26 / 2137
Permethrin#	52645-53-1	0.0023	0.00009	-	0.05	- / 6	- / 2138
Piperonyl butoxide*	51-03-6	0.24	-	0.16	0.05	2 / 10	5 / 2375
Terbutryn§	886-50-0	0.0024	-	0.005	0.01	62 / 17	64 / 12594
Tolylfluanid$	731-27-1	0.27	0.265	0.01	0.05	2 / 6	40 / 2448
Triclosan	3380-34-5	0.02	0.05	0.007	0.013	71 / 80	133 /10342

PNEC - predicted no effect concentration [µg/L]. ¥ - as stated in the EU biocide assessment report or derived from a reported NOEC by division by a factor of 50. LOQ - limit of quantification. Δ - corresponds to the EQS set in EQS-Directive 2013/39/EU (EU 2013). # also approved as (veterinary) pharmaceutical. § PPP till 2002. & PPP till 2003. $ PPP till about 2011. * used as additive in PPP.

For cybutryne (Irgarol) it was tried to evaluate whether the changes in PT approval caused a decrease of environmental concentrations (2011 phase-out for PT 7, 9, 10; currently a non-approval decision was taken for PT 21). Therefore, data from the NORMAN EMPODAT database were selected for sites with long time series over several years which mainly contained concentration values above the LOQ. Data from two sites from Germany are shown in Figure 3 (Dommitzsch, Elbe river, and Görlitz, Lausitzer Neisse river). Data from other sites/other countries were either below the LOQ or covered only short periods. At the Elbe river site cybutryne concentrations are decreasing in the period 2007 - 2013. For the tributary Lausitzer Neisse the interpretation is more difficult since the majority of the data is for the period 2007 - 2011. Data for 2012 were not available and in 2013 only a few measurements were reported. Nevertheless in recent years lower levels were detected (partly even below the LOQ). Thus the data seem to support the hypothesis that environmental levels of cybutryne are decreasing.

Figure 3 Data from the surface water monitoring of cybutryne (Irgarol) in the rivers Elbe (site Dommitzsch, upper diagram) and Lausitzer Neisse (site Görlitz, lower diagram). In each diagram an exponential fitted trend curve is displayed. Data (as µg/L) were extracted from the NORMAN EMPODAT database.





Beside data on surface waters the NORMAN data base also contains data from the monitoring of rodenticides in terrestrial biota in Sweden. The data sets cover different species, e.g., red fox and raptors such as Eurasian eagle-owls. A set of 30 samples was analysed for brodifacoum, bromadiolone, coumatetralyl, difenacoum, and warfarin. Bromadiolone was found most frequently (in 19 out of 30 samples, ranging from 18 - 1100 µg/kg wet weight). However, generally, the availability of monitoring data is low for terrestrial samples in the EMPODAT data base.

2.3 Data from the EEA surface water monitoring data base

At the web portal of the European Environment Agency (EEA) monitoring data are available from surface water monitoring programmes of European member states compiled as obliged by the Water Framework Directive (WFD) (for rivers, lakes and coastal waters). Here the data sets for river water were retrieved (EEA, 2014).

The data are covering mainly the period from approx. 2000 to 2012 and are compiled in a Microsoft Access database. Data are reported as annual average concentrations for the water phase and are usually calculated from about 4 - 12 samplings. The database was retrieved and the biocides monitoring data were extracted. The following table gives an overview over the available data (Table 4). For most compounds many data were concentrations at levels below the respective limit of quantification (LOQ). In these cases concentrations of 50 % of the LOQ are reported in accordance with the WFD requirements (Directive 2009/90/EC on the technical specifications for chemical analysis and monitoring of water status).

The data set may be evaluated in order to retrieve information on possible exceedances of PNEC and the presence of trends (especially under consideration of changes of the approval status). An example is shown in Figure 4 for the surface water monitoring data of propiconazole from Germany, where the PNEC of 6.8 µg/L was not exceeded. Propiconazole is approved as both, biocide and PPP.

The compiled EEA biocides monitoring data were tested for plausibility. In cases where the reported data are below the given LOQ they were removed (about 5 % of the EEA data). However, data sets where no LOQ is stated were kept in the Excel file (about 25 % of the EEA data). Finally, the extracted EEA biocides monitoring data were compiled in a Microsoft Excel template file provided by UBA.

Table 4: Overview over the biocides data in the EEA water data base for monitoring data from rivers (only compounds with at least 100 data sets). The respective approval status as biocide and plant protection product is also listed.

Biocide name	CAS no.	Product types	Biocide status EU (October 2015)	PPP status EU (October 2015)	No. of data sets
Acetamiprid	160430-64-8	18	review programme	approved	159
Captan	133-06-2	-	not approved	approved	930
Chlorothalonil	1897-45-6	-	not approved	approved	469
Chlorotoluron	15545-48-9	-	not approved	approved	511
Chlorpyrifos	2921-88-2	-	not approved	approved (expired in Germany)	11176
Cypermethrin	52315-07-8	8, 18	PT 8 approved, PT 18 review programme	approved	664
Diazinon	333-41-5	-	not approved	not approved	1442
Dichlofluanid	1085-98-9	7, 8, 21	PT 8 approved, PT 7, 21 review programme	not approved	378
Dichlorvos	62-73-7	-	not approved	not approved	4688
Diuron	330-54-1	7, 10	review programme	approved (expired in Germany)	11538
Fenitrothion	122-14-5	-	not approved	not approved	3506
Fenpropimorph	67564-91-4	8	approved	approved	682
Folpet	133-07-3	6, 7, 9	approved	approved	396
Imidacloprid	138261-41-3	18	approved	approved	181
Isoproturon	34123-59-6	7, 10	review programme	approved	10958
Monolinuron	1746-81-2	2	review programme	not approved	205
Naphthalene	91-20-3	-	not approved	-	9509
Permethrin	52645-53-1	8, 18	approved	not approved	1159
Prometryn	7287-19-6	-	not approved	not approved	2890
Propiconazole	60207-90-1	7, 8, 9	approved	approved	1211
Terbuthylazine	5915-41-3	-	not approved	approved	5476
Terbutryn	886-50-0	7, 9, 10	review programme	not approved	2167

PPP - plant protection product; PT - product type.

Figure 4: Overview over propiconazole monitoring data from Germany. Only sites/years with data above the LOQ were selected. Excerpt from the EEA river water data base.

Station	Year	Biocide	CASNumbe	Unit	LOQ	Minimur	Mean	Maximur	Median
BW01	2010	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.002	0.003	
BW01	2011	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.002	0.004	
BW01	2012	Propiconazole	60207-90-1	µg/l	0.001	0.002	0.002	0.003	
BW02	2010	Propiconazole	60207-90-1	µg/l	0.001	0.002	0.005	0.014	0.005
BW041	2010	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.007	0.013	0.006
BW041	2011	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.010	0.027	0.008
BW041	2012	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.005	0.010	0.005
BW05	2010	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.008	0.013	0.007
BW06	2010	Propiconazole	60207-90-1	µg/l	0.001	0.006	0.018	0.038	0.016
BW06	2011	Propiconazole	60207-90-1	µg/l	0.001	0.006	0.017	0.027	0.018
BW06	2012	Propiconazole	60207-90-1	µg/l	0.001	0.006	0.013	0.020	0.012
BW07	2010	Propiconazole	60207-90-1	µg/l	0.001	0.008	0.016	0.031	0.015
BW07	2011	Propiconazole	60207-90-1	µg/l	0.001	0.007	0.017	0.027	0.016
BW07	2012	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.014	0.025	0.013
BW08	2010	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.013	0.044	0.011
BW08	2011	Propiconazole	60207-90-1	µg/l	0.001	0.006	0.014	0.030	0.012
BW08	2012	Propiconazole	60207-90-1	µg/l	0.001	0.003	0.013	0.040	0.010
BW09	2010	Propiconazole	60207-90-1	µg/l	0.001	0.002	0.011	0.018	0.012
BW09	2011	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.012	0.031	0.012
BW09	2012	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.009	0.016	0.008
BW101	2010	Propiconazole	60207-90-1	µg/l	0.001	0.002	0.012	0.034	0.009
BW101	2011	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.013	0.027	0.012
BW101	2012	Propiconazole	60207-90-1	µg/l	0.001	0.003	0.008	0.016	0.006
BW11	2010	Propiconazole	60207-90-1	µg/l	0.001	0.002	0.012	0.036	0.008
BW131	2010	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.005	0.011	0.005
BW131	2011	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.005	0.018	0.003
BW131	2012	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.003	0.009	0.003
BW15	2010	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.008	0.021	0.007
BW16	2010	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.003	0.012	0.001
BW17	2010	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.010	0.016	0.009
BW20	2010	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.005	0.012	0.004
BW20	2011	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.005	0.012	0.005
BW20	2012	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.007	0.027	0.005
BW21	2010	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.003	0.010	0.003
BW22	2010	Propiconazole	60207-90-1	µg/l	0.001	0.002	0.003	0.007	0.003
BW24	2010	Propiconazole	60207-90-1	µg/l	0.001	0.003	0.019	0.046	0.013
BW24	2011	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.020	0.057	0.015
BW24	2012	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.012	0.031	0.009
BW25	2010	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.014	0.029	0.014
BW25	2011	Propiconazole	60207-90-1	µg/l	0.001	0.006	0.017	0.028	0.016
BW25	2012	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.013	0.021	0.013
BW26	2010	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.016	0.030	0.012
BW26	2011	Propiconazole	60207-90-1	µg/l	0.001	0.007	0.016	0.034	0.012
BW26	2012	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.015	0.033	0.011
BW27	2010	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.013	0.042	0.013
BW27	2011	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.013	0.033	0.009
BW27	2012	Propiconazole	60207-90-1	µg/l	0.001	0.001	0.009	0.024	0.008
BW28	2010	Propiconazole	60207-90-1	µg/l	0.001	0.005	0.014	0.045	0.009
BW28	2011	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.010	0.019	0.009
BW28	2012	Propiconazole	60207-90-1	µg/l	0.001	0.003	0.006	0.013	0.007
BW30	2010	Propiconazole	60207-90-1	µg/l	0.001	0.003	0.020	0.049	0.014
BW30	2011	Propiconazole	60207-90-1	µg/l	0.001	0.004	0.018	0.050	0.014
BW30	2012	Propiconazole	60207-90-1	µg/l	0.001	0.002	0.016	0.031	0.013
HH011	2012	Propiconazole	60207-90-1	µg/l	0.003	0.002	0.002	0.007	0.002
HH03	2011	Propiconazole	60207-90-1	µg/l	0.006	0.003	0.003	0.006	
HH03	2012	Propiconazole	60207-90-1	µg/l	0.003	0.002	0.002	0.006	0.002
MV02	2011	Propiconazole	60207-90-1	µg/l	0.030	0.015	0.015	0.048	
NW392	2012	Propiconazole	60207-90-1	µg/l	0.025	0.013	0.013	0.033	
RP03R	2012	Propiconazole	60207-90-1	µg/l	0.040	0.020	0.051	0.520	0.020
SH11	2011	Propiconazole	60207-90-1	µg/l	0.002	0.001	0.005	0.010	
SH12	2010	Propiconazole	60207-90-1	µg/l	0.040	0.020	0.020	0.050	
SH13	2011	Propiconazole	60207-90-1	µg/l	0.006	0.003	0.003	0.007	
SH16	2011	Propiconazole	60207-90-1	µg/l	0.006	0.003		0.007	
SN01	2012	Propiconazole	60207-90-1	µg/l	0.015	0.008	0.008	0.022	0.008
SN02	2011	Propiconazole	60207-90-1	µg/l	0.015	0.008	0.008	0.033	0.008
SN02	2012	Propiconazole	60207-90-1	µg/l	0.015	0.008	0.008	0.034	0.008
SN03	2012	Propiconazole	60207-90-1	µg/l	0.015	0.008	0.008	0.033	0.008

2.4 Time trend evaluation of SPM monitoring data

As discussed in Rüdel and Fliedner (2014b, Annex 3) suspended particulate matter (SPM) and (surface) sediments may be investigated for biocides which tend to adsorb or bind to inorganic and organic particles and materials. Such compounds are often not detected in the water phase monitoring (concentrations potentially low due to low solubility). SPM can be sampled as an alternative to sediments (Schubert et al. 2012). It may be viewed as a surrogate of surface sediment (re-mobilised upstream surface sediment and/or material which is expected to be deposited downstream the sampling site). Thus SPM can be assumed being a sink for adsorbing biocides similar to sediment. For a trend monitoring SPM samples seem to be more appropriate since SPM can be sampled more reproducibly as compared to sediment. At least in rivers sediment is prone to re-mobilisation by flood events. SPM is covered by the routine monitoring of some German federal states. Archived SPM samples are also available from the German environmental specimen bank (ESB; www.umweltprobenbank.de/en) for retrospective monitoring studies. For further information on SPM monitoring refer to Rüdel and Fliedner (2014b, Annex 3).

From a previous study data on the concentrations of cybutryne (Irgarol), propiconazole, and tebuconazole in SPM are available (Schulz 2013). During the present study SPM samples were investigated for levels of triclosan and methyl-triclosan (see sub-report by Schwarzbauer and Wluka 2015, Annex 4, confidential). In both studies samples were applied from the archive of the German ESB. SPM is sampled for the ESB programme at several riverine sites in Germany since 2005/2006. Annual homogenates of monthly samples are freeze-dried and stored at low temperatures. For the studies time series of sub-samples from several sampling sites were applied. Analytical details are described in Schulz et al. (2013) and Schwarzbauer and Wluka (2015, Annex 4).

The time trend data were statistically evaluated with the Microsoft Excel-based software tool LOESS-Trend, Version 1.1 provided by J. Wellmitz (UBA, Dep. II 2.5). This tool fits a locally weighted scatterplot smoother (LOESS, with a fixed window width of 7 years) through the yearly concentration levels. It also tests for significance of linear and non-linear trend components by means of an analysis of variance (ANOVA). For more information refer to Koschorreck et al. (2015).

The data are summarised in Table 5. Representative data are shown in Figure 5- Figure 7.

Only a few of the time trends were significant at a level of $p < 0.05$. Highly significant linear decreasing trends of cybutryne levels were observed, e.g., at the sites Saar / Rehlingen and Rhine / Koblenz (for the investigated period a decrease by -91 % and -70 %, respectively). Clear changes of concentration levels over time were also obvious at most other sites for cybutryne although trends were not significant. In most cases lower concentration levels were observed in recent years. For propiconazole and tebuconazole the results were varying. At the site Elbe / Blankenese clearly higher levels were observed for tebuconazole in recent years as compared to the earlier years of the time series (+68 % over the whole period). However, at most other sites tebuconazole concentrations were decreasing (Table 5).

For triclosan non-significant increasing trends were detected at both investigated sites (Saar / Güdingen and Saale / Wettin). Interestingly the trends for methyl-triclosan are decreasing (also not significant). Generally, the averaged levels of triclosan are higher than those of methyl-triclosan (about factor 20) and cybutryne, tebuconazole and propiconazole (factors of about 20 - 100). Similar SPM levels were reported by Sengl (2012) for a study in SPM from Bavarian rivers (triclosan up to 125 µg/kg dry weight, methyl-triclosan up to about 25 µg/kg dry weight).

For fish monitoring data also decreasing methyl-triclosan values were reported for the period from about 2003 to 2008 (Rüdel et al. 2013; triclosan data were not available for that period). The detection of triclosan in SPM stands in contradiction to an earlier investigation by FU Berlin (Rüdel et al.

2013). In that study triclosan was reported to be < 0.1 µg/kg in several ESB SPM samples from the period 2005 - 2007. For methyl-triclosan levels of about 1 - 5 µg/kg were reported (lower than in the study by Schwarzbauer and Wluka 2015, Annex 4). It seems that the method applied in the earlier study has not been appropriate. However, as discussed in Rüdel et al. (2013) the results from earlier studies on triclosan and methyl-triclosan levels of sediments and SPM generally had been very heterogeneous.

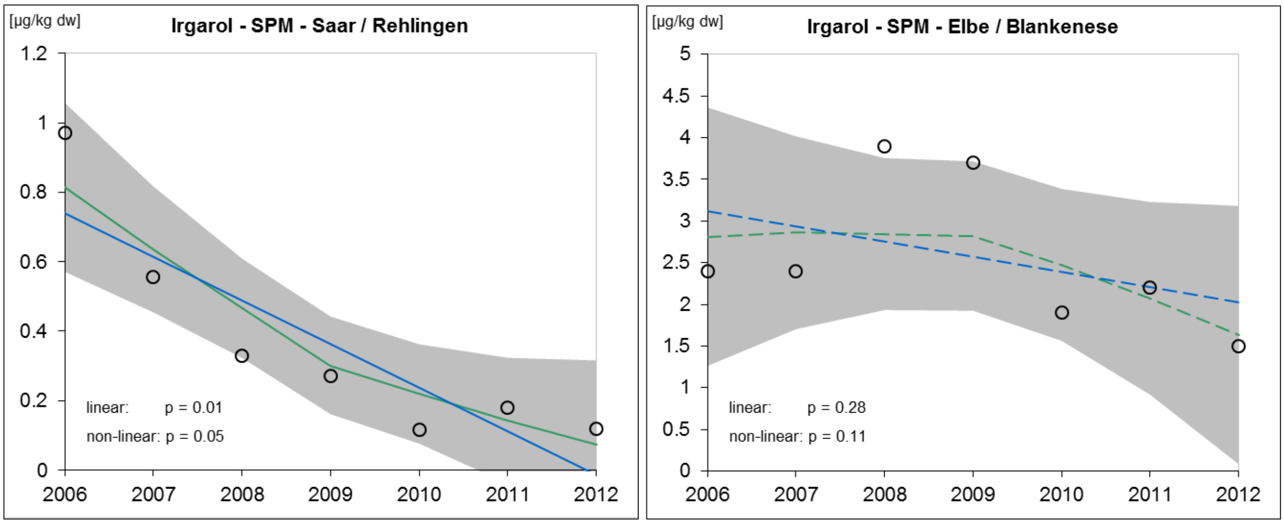
Table 5: Overview over the trend evaluation of the SPM concentration data for cybutryne, propiconazole, tebuconazole, triclosan and methyl-triclosan using the LOESS-Trend tool.

Site	Linear trend	p-value	Non-linear trend	p-value	change per year [µg/kg]	total change [%]
Cybutryne (Irgarol)						
Saar / Rehlingen	significant	0.01#	significant	0.05#	-0.1	-91
Rhine / Koblenz	significant	0.01#	not signif.	0.37	-0.1	-70
Rhine / Bimmen	not signif.	0.13	not signif.	0.22	-0.1	-56
Elbe / Blankenese	not signif.	0.28	not signif.	0.11	-0.2	-42
Elbe / Zehren	not signif.	0.84	not signif.	0.14	-0.0	-17
Saale / Wettin	not signif.	0.23	not signif.	1.00	-0.3	-88
Propiconazole						
Saar / Rehlingen	not signif.	0.82	not signif.	0.26	-0.0	-1
Rhine / Koblenz	not signif.	0.40	not signif.	0.11	-0.1	-18
Rhine / Bimmen	significant	< 0.01#	not signif.	1.00	-0.3	-71
Elbe / Blankenese	not signif.	0.22	not signif.	0.79	-0.1	-22
Elbe / Zehren	not signif.	0.76	not signif.	1.00	+0.0	+7
Saale / Wettin	not signif.	0.29	not signif.	1.00	-0.3	-40
Tebuconazole						
Saar / Rehlingen	not signif.	0.70	not signif.	0.06	-0.0	-4
Rhine / Koblenz	not signif.	0.45	not signif.	0.66	-0.0	-19
Rhine / Bimmen	significant	0.02#	not signif.	0.38	-0.3	-82
Elbe / Blankenese	not signif.	0.09	not signif.	0.34	+0.1	+68
Elbe / Zehren	not signif.	0.91	not signif.	0.07	-0.0	+0
Saale / Wettin	not signif.	0.22	not signif.	1.00	-0.3	-42

Site	Linear trend	p-value	Non-linear trend	p-value	change per year [µg/kg]	total change [%]
Triclosan						
Saar / Güdingen	not signif.	0.16	not signif.	0.71	+4.7	+27
Saale / Wettin	not signif.	0.06	not signif.	0.58	+4.8	+53
Methyl-triclosan						
Saar / Güdingen	not signif.	0.35	not signif.	0.16	-0.1	-15
Saale / Wettin	not signif.	0.52	not signif.	0.10	-0.2	-13

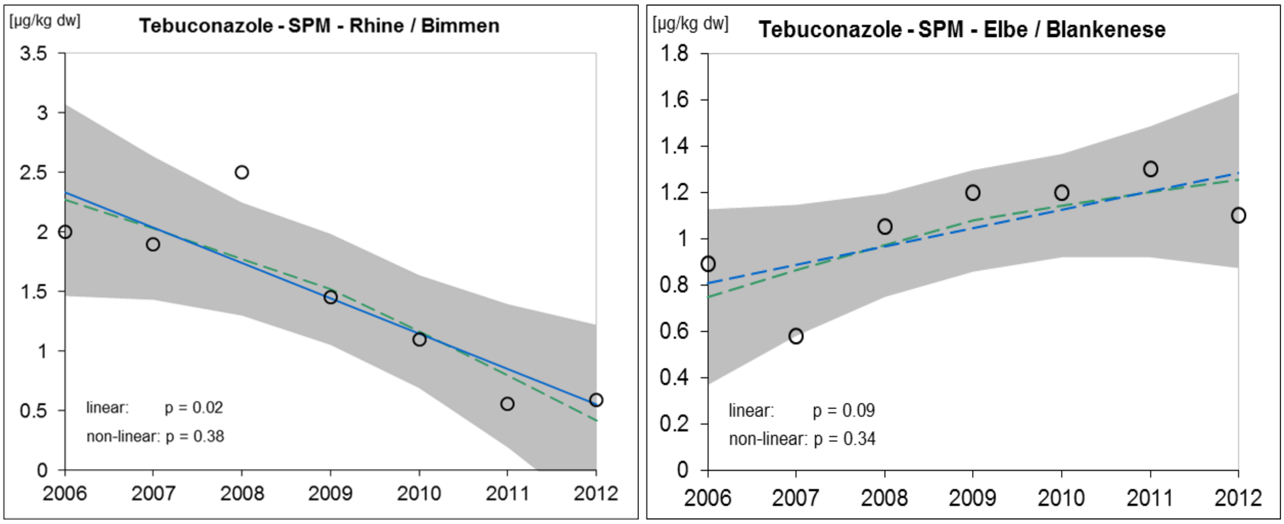
Bold: increasing trend. # significant trend (p ‹ 0.05).
Data sources: Schulz et al. (2013), Schwarzbauer and Wluka (2015, Annex 4).

Figure 5: Examples for the trend evaluation of the SPM concentration data for cybutryne (Irgarol) using the LOESS-Trend tool. Data are in µg/kg dry weight. Significant trends are shown as solid lines, non -significant as dashed ones. Left: Saar / Rehlingen. Right: Elbe / Blankenese.



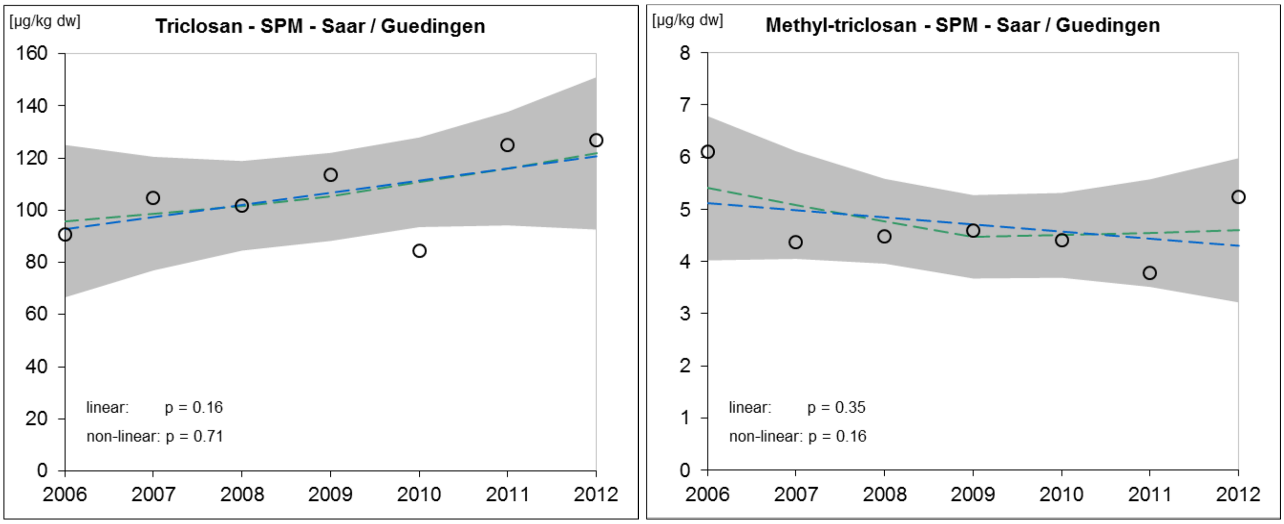
Data source: Schulz et al. (2013).

Figure 6: Examples for the trend evaluation of the SPM concentration data for tebuconazole using the LOESS-Trend tool. Data are in µg/kg dry weight.
Significant trends are shown as solid lines, non -significant as dashed ones.
Left: Rhine / Bimmen. Right: Elbe / Blankenese.



Data source: Schulz et al. (2013).

Figure 7: Examples for the trend evaluation of the SPM concentration data for triclosan and methyl-triclosan for the site Saar / Güdingen using the LOESS-Trend tool. Data are µg/kg dry weight.
Significant trends are shown as solid lines, non -significant as dashed ones.
Left: triclosan. Right: methyl-triclosan.



Data source: Schwarzbauer and Wluka (2015, Annex 4).

3 Plausibility of the prioritisation approach

3.1 Scope of evaluation

The results from measurements conducted in this project are provided and discussed in the following sub-reports: “Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measures”, Schwarzbauer and Wluka (2015, Annex 4); “Determination of Rodenticides in Fish Samples of the German Environmental Specimen Bank”, Kotthoff et al. (2015, Annex 5); “Determination of triclosan and methyl-triclosan in soil and earthworm samples from sewage sludge-treated agricultural sites”, Kharel et al. (2015, Annex 6).

An overview on the evaluated literature on biocides monitoring (scientific publications and studies/ reports from government agencies and other institutions) is provided in the main report (Rüdel et al. 2015). Monitoring data sets obtained from databases (NORMAN, EEA) or provided by LfU are described in section 2 of the present report (Annex 7).

Here it will be evaluated whether the available monitoring data support the applicability of the proposed prioritisation approach and monitoring concept.

3.2 Are the results from the exemplarily performed experimental monitoring studies in consistence with the prioritisation approach?

The selection of the experimental studies to be conducted in this project was not based on the prioritisation scheme but on the demand on data for the selected biocidal compounds. For example, rodenticides are of high concern due to their persistence and bioaccumulation potential. For azole fungicides the reason for inclusion in this study was the recent change of approval of cybutryne (Irgarol) for certain biocidal product types and the consequences for the use of possible substitute chemicals. The experimental study should provide information on changes of concentration levels in environmental media induced by the regulatory decision.

In the experimental study by Schwarzbauer and Wluka (2015, Annex 4) the following compounds were covered: triclosan, methyl-triclosan, cybutryne (Irgarol), propiconazole, tebuconazole, imazalil, thiabendazole, and cyproconazole. The investigated matrices were wastewater, sewage sludge and surface water. Additionally SPM from the German environmental specimen bank archive was retrieved and analysed for triclosan/methyl-triclosan. All investigated compounds were also covered in the prioritisation approach (i.e. EU biocide assessment reports are available; methyl-triclosan as relevant transformation product of triclosan was covered in the triclosan report). Thus it is possible to compare the outcome of the prioritisation for the different matrices with the experimental results.

Prioritisation outcome for **surface waters** (under consideration of compounds which are also approved as PPPs like tebuconazole, propiconazole and imazalil): from the investigated set of compounds only triclosan (rank 2), methyl-triclosan (5), and tebuconazole (12) were ranked in the TOP 15 list. However the prioritisation was based on the approval situation in spring 2014. In the meantime non-approval decisions were taken for triclosan usage in PT 2, 7 and 9 (and recently for the remaining PT 1, too). As a consequence triclosan/methyl-triclosan are now ranked only as less relevant for a monitoring. Since the samplings overlap with the phase-out period (phase-out until April 2015), lower findings of triclosan/methyl-triclosan as compared to similar studies in previous years (e.g., von der Ohe et al. 2012 with data from the period 2006 - 2008) may be explained by reduced consumption. Tebuconazole was detected at sampling sites downstream of two sewage treatment plants (STPs) by Schwarzbauer and Wluka (2015, Annex 4).

Prioritisation outcome for **STP effluents** (under consideration of compounds which are also approved as PPPs; triclosan/methyl-triclosan would also not be on the TOP 15 ranking list if the recent changes of PT approval were considered; see above): from the set of compounds investigated by Schwarzbauer and Wluka (2015, Annex 4) only triclosan (rank 1), methyl-triclosan (3) were on the generated list of biocides relevant for a monitoring. In the experimental study by Schwarzbauer and Wluka (2015, Annex 4) the following compounds (covered in the prioritisation approach but not prioritised) were detected at least in some of the STP effluents: imazalil, methyl-triclosan, cyproconazole, propiconazole, tebuconazole, thiabendazole (only trace amounts).

Prioritisation outcome for **sewage sludge** (under consideration of compounds which are also approved as PPPs): none of the compounds covered by the study by Schwarzbauer and Wluka (2015, Annex 4) was on the ranking list for sewage sludge. In the sludge samples only cyproconazole was detected by Schwarzbauer and Wluka (in relatively high amounts of up to 380 ng/g dry weight). Cyproconazole was not ranked due to a low K_{OC} given in the EU biocide assessment report (below the K_{OC} criterion of 10000 L/kg set as threshold for compounds relevant for sludge adsorption in the prioritisation scheme; Rüdel and Fliedner 2014a, Annex 2).

Prioritisation outcome for **sediment/suspended particulate matter** (only triclosan/methyl-triclosan investigated by Schwarzbauer and Wluka 2015, Annex 4; all PTs were considered since the retrospective monitoring covers samples taken before 2014): neither triclosan nor methyl-triclosan were on the ranking list for suspended particulate matter (SPM). However, in all SPM samples both triclosan and methyl-triclosan were detected. The reason that the compounds were not considered for the SPM monitoring was the low experimentally determined K_{OC} values provided in the EU triclosan assessment report (below the K_{OC} criterion of 10000 L/kg set as threshold for compounds relevant for SPM monitoring in the prioritisation scheme; Rüdel and Fliedner 2014a, Annex 2). The values estimated by quantitative structure-activity relationship (QSAR) models retrieved from the EPI Suite tool (US EPA 2012) were higher (even > 10000 L/kg depending on the applied QSAR model). If the QSAR derived K_{OC} values were applied both compounds were listed among the TOP 10 compounds prioritised for SPM monitoring. It is recommended to verify the low experimental K_{OC} values for triclosan and methyl-triclosan reported in the EU biocide assessment report. In case of triclosan it may also be possible that the K_{OC} value is not appropriate to describe the binding to SPM. Under environmental pH values triclosan also exists both as neural compound and as anion. As anion it may bind at cationic sites on SPM.

Triclosan and methyl-triclosan were also investigated in **soil and terrestrial biota** (earthworm from sewage-sludge treated sites Kharel et al. 2015, Annex 6). However, for soil triclosan and methyl-triclosan were not among the prioritised compounds (here previous triclosan usage in all relevant PTs was considered since sludge applications were accumulative over a period of several years). The probable reason again are the low K_{OC} values provided in the EU triclosan assessment report. If the higher QSAR derived K_{OC} values were applied, both compounds were highly ranked for the soil compartment. The prioritised biocides for the terrestrial biota monitoring covered both triclosan and methyl-triclosan (rank 1 and 2, respectively). Thus the ranking seems to be consistent with the experimental monitoring findings.

In a further experimental study anticoagulant rodenticides levels were determined in fish liver tissue (Kotthoff et al. 2015, Annex 5). All investigated substances (brodifacoum, bromadiolone, chlorophacinone, coumatetralyl, difenacoum, difethialone, flocoumafen, and warfarin) were also covered in the prioritisation approach (Rüdel and Fliedner 2014a, Annex 2). However, all of these compounds were ranked lower in the prioritisation list for aquatic biota (or were not ranked at all due to a reported BCF below 2000 L/kg, e.g., as for chlorophacinone, coumatetralyl or warfarin; this value was set as filter criterion). Nevertheless, the compounds frequently detected in fish liver by Kotthoff et al. (2015, Annex 5), brodifacoum, bromadiolone and difethialone, fulfil the criteria and were contained in the list (although with lower scores).

3.3 Do the available monitoring data support the applicability of the proposed prioritisation approach?

In the data set provided by the Bavarian Environment Agency (LfU; section 2.1) the following biocidal compounds were detected above the limit of quantification (LOQ) in > 3 % of surface water samples (for compounds which are currently approved as biocide but not as PPP in Europe): chlorotoluron, cybutryne (Irgarol), diuron, triclosan. Permethrin was measured but the applied LOQ was higher than the PNEC given in the respective EU biocide assessment report (the same holds true for, e.g., cyfluthrin and cypermethrin which are not considered here because of their PPP approval; Table 1). However, only for permethrin, cybutryne and triclosan EU assessment reports were available during the project so that the other compounds currently are not considered for the prioritisation. Triclosan was ranked high in the prioritisation list for surface water monitoring. Permethrin was also contained in the TOP 10 prioritisation list. Cybutryne, on the other hand, was ranked low due to the current usage in only one product type. However, at least in larger water bodies with leisure boats or transport traffic cybutryne could have a higher relevance. It may be considered to weight in the assessment approach the usage in PT 21 higher or to consider antifouling biocides separately (e.g., for monitoring at marinas; see also Rüdel and Fliedner (2014b, Annex 3).

From the biocidal compounds without current PPP approval covered by the NORMAN database (Table 3) again not all were covered in prioritisation approach due to missing EU biocide assessment reports. Thus, e.g., terbutryn and o-benzyl-p-chlorophenol (clorophene) could not be assessed. From the remaining compounds cybutryne, permethrin, and triclosan were already discussed above. Dichlofluanid and tolylfluanid were also among the TOP 10 compounds on the prioritisation list for surface water. Cyfluthrin was not prioritised due to a high K_{OC} (filter criterion 100000 L/kg). N,N-diethyltoluamide (DEET) was assessed as not relevant due to the high PNEC stated in the assessment report. The large difference between the derived PNECs and the actual quantified levels (Table 3) seems to support this assessment for DEET.

Generally, the results of the prioritisation approach showed a moderate agreement with the available monitoring data. This seems to be due to the fact that, so far, not all relevant biocides could be used for prioritisation due to the lack of EU biocides assessment reports for several compounds. Another aspect is that the data extracted from the evaluation reports do not always appear plausible. An adjustment of the prioritisation may be considered for antifouling compounds. For these biocides in the prioritisation approach a higher weighting of the direct entry into the aquatic environment may be required.

3.4 Are the biocides covered by the Water Framework Directive monitoring also identified as relevant by the prioritisation approach?

Several biocides are already covered by the WFD (EC 2000) surface water monitoring or in Germany as national relevant pollutants by the German Surface Water Ordinance (OGewV, 2011). The respective compounds are listed in Table 6. However, currently only cybutryne, cypermethrin, and propiconazole were covered in the biocides monitoring prioritisation proposal (Rüdel und Fliedner 2014a, Annex 2). Cybutryne was only ranked low in the prioritisation list for water phase monitoring as discussed before. Cypermethrin and propiconazole, both also approved as PPPs, had a medium relevance for the water phase monitoring. Due to a high K_{OC} cypermethrin was identified as relevant for a monitoring in suspended particulate matter or sediment.

Recently a watch list with 10 compounds/groups of compounds was established in the WFD context. For these chemicals additional monitoring data shall be gathered ((EU) 2015/495; EU 2015). On this list also 5 neonicotinoid compounds are covered: imidacloprid (CAS no. 105827-78-9/138261-41-3), thiacloprid (CAS no. 111988-49-9), thiamethoxam (CAS no. 153719-23-4), clothianidin (CAS no.

210880-92-5), acetamiprid (CAS no. 135410-20-7/160430-64-8). These five compounds are all both biocides and PPPs. Except for thiacloprid all compounds were already included in the group of compounds applied for the prioritisation approach. However, according to the criteria applied for prioritisation (Rüdel und Fliedner 2014a, Annex 2) these compounds were assessed as less relevant regarding emissions, effects and relevance for the water phase monitoring (also not relevant for a SPM/sediment monitoring due to low K_{OC}). The reason for the consideration of the neonicotinoids for the WFD monitoring may be due to the PPP use of the compounds.

Table 6: Biocides included in the EU biocides review programme covered by surface water monitoring according to WFD (2000/60/EC, EC 2000) and daughter directives (2008/105/EC, EC 2008 and 2013/39/EU, EU 2013) or a German national regulation (German Surface Water Ordinance, OGewV 2011).

Biocide name	CAS no.	PT	Monitoring obligation	Comment
Cybutryne	28159-98-0	Non-approval decision	2013/39/EU	AA and MAC EQS water; to be monitored by Dec. 2018
Cypermethrin#	52315-07-8	8, 18	2013/39/EU	AA and MAC EQS water; to be monitored by Dec. 2018
Dichlorvos	62-73-7	Non-approval decision	2013/39/EU; OGewV 2011	AA and MAC EQS water; to be monitored by Dec. 2018
Diuron#	330-54-1	7, 10	2008/105/EC; 2013/39/EU	AA and MAC EQS water
Isoproturon#	34123-59-6	7, 10	2008/105/EC; 2013/39/EU	AA and MAC EQS water
Naphthalene	91-20-3	Non-approval decision	2008/105/EC; 2013/39/EU	AA and MAC EQS water; 2013/39/EU states lower EQS as compared to 2008/105/EC
Terbutryn	886-50-0	7, 9, 10	2013/39/EU	AA and MAC EQS water; to be monitored by Dec. 2018
Chlorotoluron#	15545-48-9	Non-approval decision	OGewV 2011	AA EQS water
Diazinon	333-41-5	Non-approval decision	OGewV 2011	AA EQS water
Fenitrothion	122-14-5	Non-approval decision	OGewV 2011	AA EQS water
Monolinuron	1746-81-2	2	OGewV 2011	AA EQS water
Prometryn	7287-19-6	Non-approval decision	OGewV 2011	AA EQS water
Propiconazole#	60207-90-1	7, 8, 9	OGewV 2011	AA EQS water
Terbuthylazine#	5915-41-3	Non-approval decision	OGewV 2011	AA EQS water

also approved as plant protection product. AA - annual average, EQS - environmental quality standard; MAC - maximum allowable concentration; PT - biocides product type.

3.5 Main conclusions on the applicability of the prioritisation and outlook

An important criterion for the assessment of the performance of the prioritisation approach is whether the available monitoring data support the applicability of the proposal. This would be the case if the list of the prioritised biocides for a compartment would match with the list of compounds detected in monitoring programmes for this compartment. However, as discussed above the results of the prioritisation approach showed only a moderate agreement with the compounds detected in German and European monitoring programmes.

Another assessment aspect is whether there is a congruence of the prioritisation results with those compounds covered by current monitoring activities (which are also resulting from a prioritisation process). In Europe the WFD monitoring is of prime relevance since it is the broadest monitoring activity. However, only three biocides which currently covered as WFD priority compounds, i.e. cybutryne, cypermethrin, and propiconazole, could be considered in the prioritisation approach (Rüdel und Fliedner 2014a, Annex 2). The latter compounds were not ranked high in the proposed prioritisation approach but the consideration of cypermethrin and propiconazole for the WFD monitoring may be justified by the use of these compounds as PPPs, too.

To conclude, the assessment of the performance of the prioritisation scheme is hindered by limited information. On the one hand only a fraction of the relevant biocides (mostly already approved compounds) are currently covered in the prioritisation approach. For a larger fraction of compounds no EU biocide assessment reports were available (status of the prioritisation: March 2014). On the other hand biocides are up to now not adequately considered in monitoring programmes (as compared, e.g., to active ingredients applied as PPPs). Available monitoring data mainly cover surface waters while findings for soil and groundwater are almost totally absent for biocides. Thus there is only a limited overlap of biocides which are in the set applied for the prioritisation and those for which monitoring data are available. Best information is available for the water compartment. For the prioritised compounds for which monitoring data are available the evaluation shows that the performance of the prioritisation scheme is moderate. Partly the monitoring data confirm the prioritisation approach, but in other cases prioritised compounds are not detected or detected compounds were not prioritised.

Potential for improvement of the prioritisation approach:

- Update of the biocides database for the prioritisation since in recent months several additional EU biocides assessment reports were published.
- Biocides for which no assessment reports are available but which were already detected in monitoring studies may be considered in the prioritisation approach preliminary on basis of data from public databases or QSAR estimations; in cases where these compounds are also applied as PPPs data from the PPP assessment reports may be available, too.
- A weak point in the prioritisation approach is the assessment of the exposure relevance which is currently operationalised as usage of the respective biocide in certain biocidal product types and on the number of products on the market; the use of consumption data for biocides in the prioritisation scheme would probably allow a better assessment of the exposure relevance (refer to discussion on proposed additional reporting requirements in Pohl et al. 2015, Annex 8).
- An adjustment of the prioritisation approach may be considered for antifouling compounds. For these biocides a higher weighting of the direct entry into the aquatic environment may be required in the prioritisation approach in order to consider the exposure relevance appropriately.
- It is important to note that the lists of compounds as suggestion for monitoring authorities should be refined further in discussion between regulatory and monitoring experts. Beside the results from the prioritisation approach also biocides already detected in monitoring studies should be considered in the refinement (if the environmental findings can be related to the biocide use).

The prioritisation of biocides according to the proposed scheme is a dynamic process since changes in the product type approval for a biocide cause a change of the emission relevance and the relevance for certain environmental compartments. Thus it is recommended to update the compound data base regularly to consider approval/non-approval decisions for already covered compounds. If EU assessment reports for additional substances become available the properties data and product type approval information for the respective compounds should also be added to the prioritisation database.

4 References

EC (2000): Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal of the European Communities, L 327/1, 22.12.2000. http://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=PDF

EC (2008): Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. Official Journal of the European Union, L 348/84, 24.12.2008. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:348:0084:0097:EN:PDF

EC (2009): Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status. OJ L 201, 1.8.2009, p. 36-38. http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1445005151598&uri=CELEX:32009L0090

EEA (2014): Waterbase - Rivers, v14. Microsoft Access File. European Environment Agency (EEA), Copenhagen, Denmark. www.eea.europa.eu/data-and-maps/data/waterbase-rivers-10

EU (2013): Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy Text with EEA relevance. OJ L 226, 24.8.2013, p. 1-17. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013L0039&qid=1446142648497&from=EN

EU (2015): Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. OJ L 78, 24.3.2015, p. 40-42. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32015D0495&qid=1446147855881&from=EN

Koschorreck J, Heiss C, Wellmitz J, Fliedner A, Rüdel H (2015): The use of monitoring data in EU chemicals management--experiences and considerations from the German environmental specimen bank. Environ Sci Pollut Res 2015, 22, 1597-1611.

Kotthoff M, Jürling H, Bücking M, Rüdel H (2015): Determination of Rodenticides in Fish Samples of the German Environmental Specimen Bank. Sub-report (Annex 5) on project (FKZ) 3712 67 403 "Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment" on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

OGewV (2011): Verordnung zum Schutz der Oberflächengewässer (Oberflächengewässerverordnung - OGewV) vom 20. Juli 2011. (German Surface Water Ordinance). Bundesgesetzblatt Jahrgang 2011 Teil I Nr. 37, 1429-1469. 25. Juli 2011. http://www.gesetze-im-internet.de/bundesrecht/ogewv/gesamt.pdf

Pohl P, Dulio V, Botta F, Schwarzbauer J, Rüdel H (2015): Environmental monitoring of biocides in Europe - compartment-specific strategies. Workshop Report (June 25-26, 2015 in Berlin). Sub-report (Annex 8) on project (FKZ) 3712 67 403 "Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment" on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Rüdel H, Fliedner A (2014a): Überprüfung, Überarbeitung und Vervollständigung des vorläufigen Priorisierungs-/Monitoring-Konzepts. Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany. Sub-report (Annex 2) on project (FKZ) 3712 67 403 "Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment" on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Rüdel H, Fliedner A (2014b): Design of a Biocide Monitoring Programme. Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany. Sub-report (Annex 3) on project (FKZ) 3712 67 403 "Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment" on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Rüdel H, Fliedner A, Schwarzbauer J, Wluka A (2015): Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment. Report on project (FKZ) 3712 67 403 on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Schubert B, Heininger P, Keller M, Ricking M, Claus E (2012): Monitoring of contaminants in suspended particulate matter as an alternative to sediments. Trends Anal. Chem. 36, 58-70.

Schulz, V (2013): Zeitreihenuntersuchung von Irgarol und den Azolfungiziden Tebuconazol und Propiconazol in Schwebstoffproben der Umweltprobenbank des Bundes (UPB). Projektnummer (28 221). FOOD GmbH Jena Analytik-Consulting, Jena, Germany for Umweltbundesamt, Dessau-Rosslau, Germany.
www.umweltprobenbank.de/en/documents/publications/21443

Schwarzbauer J, Wluka A (2015): Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measures. EMR Energy & Mineral Resources Group, Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Aachen, Germany. Sub-report (Annex 4) on project (FKZ) 3712 67 403 "Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment" on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany.

Sengl M (2012): Monitoring of selected biocides - experiences from Bavaria. Bavarian Environment Agency, Augsburg, Germany. Presentation during the UBA NORMAN Workshop on Biocides Monitoring, Berlin, Germany, November 2012.

Kharel S, Kotthoff M, Rüdel H (2015): Determination of triclosan and methyl-triclosan in soil and earthworm samples from sewage sludge-treated agricultural sites. Sub-report (Annex 6) on project (FKZ) 3712 67 403 "Development of cornerstones for a monitoring programme for the assessment of biocide emissions into the environment" on behalf of Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau, Germany

US EPA (2012): EPI Suite v4.11 (Estimation Programs Interface), November, 2012. U.S. Environmental Protection Agency, Exposure Assessment Branch, Washington, DC, USA

von der Ohe PC, Schmitt-Jansen M, Slobodnik J, Brack W (2012): Triclosan--the forgotten priority substance? Environ Sci Pollut Res 19, 585-591

Wenzel A, Schlich K, Shemotyuk L, Nendza M (2015): Revision der Umweltqualitätsnormen der Bundes-Oberflächengewässerverordnung nach Ende der Übergangsfrist für Richtlinie 2006/11/EG und Fortschreibung der europäischen Umweltqualitätsziele für prioritäre Stoffe. Fraunhofer-Institut for Molecular Biology and Applied Ecology, Schmallenberg, Germany and Analytisches Laboratorium für Umweltuntersuchungen und Auftragsforschung, Luhnstedt, Germany. UBA-Texte 47/2015. Umweltbundesamt, Dessau-Rosslau, Germany. https://www.umweltbundesamt.de/publikationen/revision-der-umweltqualitaetsnormen-der-bundes

Appendix 1: NORMAN fact sheet Triclosan (October 2015)

Substance factsheets of chemical pollutants

Identification and Summary Information

Substance: Triclosan

CAS no: 3380-34-5

Categorisation (use category I): Personal care products / Biocides

Categorisation (use category II):

Categorisation (use sub-category I):

Categorisation (use sub-category II):

Total no of analyses: 14294

% of analyses with values above LoD: 84,01%

% of analyses with values above LoQ: 65,75%

No of stations: 1104

No of countries: 12

Description of substance and references

n.a.

Detailed Information

Data availability by countries

Country	No. of stations	No. of analyses
Austria	6	13
Bulgaria	5	11
France	289	1435
Germany	682	12609
Greece	1	3
Hungary	30	72
Italy	45	50
Romania	15	38
Slovakia	6	12
Slovenia	7	7
Sweden	17	38
United Kingdom	1	6

No. of analyses by year

Country	0	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2005	2006	2007	2008	2009	2010	2011	2012	2013
Austria	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6
Bulgaria	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5
France	66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	953	416	0
Germany	6	2	4	12	3	11	2	11	14	16	17	0	2075	2168	2088	1618	1618	1636	1302	6
Greece	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0
Hungary	42	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30
Italy	0	0	0	0	0	0	0	0	0	0	0	0	29	21	0	0	0	0	0	0
Romania	23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	15

Country	0	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2005	2006	2007	2008	2009	2010	2011	2012	2013
Slovakia	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6
Slovenia	0	0	0	0	0	0	0	0	0	0	0	7	0	0	0	0	0	0	0	0
Sweden	0	0	0	0	0	0	0	0	0	0	0	0	0	7	1	0	0	0	0	30
United Kingdom	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6	0	0	0	0	0

Data availability according to analysed ecosystem/matrix and basic statistical information

Matrix	Total No. of analyses	No. of analyses above LoQ	Max	Median	Unit	Lowest PNEC	EQS
Water - Surface water - River water	12888	10342	3.06	0.013	µg/l	0.02	n.a.
Water - Surface water - Lake water	186	133	0.18	0.007	µg/l	0.02	n.a.
Water - Ground water	953				µg/l	0.02	n.a.
Water - Waste water - Industrial	6	6	0.046	0.04	µg/l	0.02	n.a.
Water - Waste water - Municipal	12	12	0.13	0.0705	µg/l	0.02	n.a.
Water - Waste water - Other	1	1	0.0052	0.0052	µg/l	0.02	n.a.
Sediments - River water	112	5	65	28.7	µg/kg dry weight	7.65	n.a.
Sediments - Lake water	22	4	290	36.5	µg/kg dry weight	7.65	n.a.
Suspended matter - Other	1	1	1410	1410	µg/kg dry weight	n.a.	n.a.
Sewage sludge - Industrial	1	1	1200	1200	µg/kg dry weight	n.a.	n.a.
Sewage sludge - Municipal	8	8	3800	1700	µg/kg dry weight	n.a.	n.a.
Sewage sludge - Other	6	6	4800	3350	µg/kg dry weight	n.a.	n.a.
Biota - River water	90	35	31	0.49	µg/kg wet weight	3.04	n.a.
Biota - Lake water	8	3	52	4.1	µg/kg wet weight	3.04	n.a.

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Environmental monitoring of biocides in Europe - compartment-specific strategies
Workshop Report, June 25–26, 2015 in Berlin (Annex 8)

by

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Kurzbeschreibung

Die Umsetzung der europäischen Verordnung über die Bereitstellung auf dem Markt und die Verwendung von Biozidprodukten (EU Nr. 528/2012) verursacht Änderungen im Gebrauch von Biozidwirkstoffen und deren Eintrag in die Umwelt. Einige Stoffe wurden bereits vom Markt genommen oder können in Kürze als Folge von Nichtzulassungsentscheidungen nicht mehr angewandt werden. Darüber hinaus wird die Verwendung bestimmter Biozidwirkstoffe durch Risikominderungsmaßnahmen eingeschränkt werden. Für solche Stoffe werden abnehmende Konzentrationen in der Umwelt erwartet. Auf der anderen Seite können die Umweltkonzentrationen anderer Biozide, die als Ersatz für nicht mehr zugelassene Verbindungen dienen, ansteigen. Umweltmonitoring kann helfen zu beurteilen, ob die Umsetzung der Verordnung positive Auswirkungen auf die Umweltqualität hat (z.B. geringere Umweltkonzentrationen von Bioziden, für die Risikominderungsmaßnahmen eingeführt wurden). In diesem Kontext organisierte das Umweltbundesamt in Zusammenarbeit mit dem NORMAN-Netzwerk im Juni 2015 in Berlin einen internationalen Workshop. Die Diskussionen konzentrierten sich insbesondere auf kompartimentspezifische Monitoringansätze und behandelten Aspekte wie Priorisierung, Probenahmeverfahren, Messungen und Datenbanken. Mehr als 70 Workshop-Teilnehmer aus mehr als einem Dutzend europäischer Staaten, die Behörden, Forschungsinstitute und Universitäten, Industrie und Industrieverbände sowie Nichtregierungsorganisationen repräsentierten, nahmen an den Diskussionen der 13 Vorträge, 13 Poster und drei Arbeitsgruppen teil. Dieser Bericht dokumentiert die Workshop-Diskussionen und Kurzfassungen der Beiträge sowie die wichtigsten gezogenen Schlussfolgerungen.

Abstract

The implementation of the European regulation concerning the making available on the market and use of biocidal products (EU No 528/2012) causes changes in the application of biocidal active substances and their entry into the environment. Some substances have already been withdrawn from the market, or may be withdrawn soon as a consequence of non-approval decisions. Additionally, the use of certain biocidal substances will be restricted by risk mitigation measures. For these compounds decreasing concentrations in the environment are expected. On the other hand, environmental levels of other biocides may rise as a result of replacement of non-approved compounds. Environmental monitoring can help in assessing whether the implementation of the regulation has positive effects on environmental quality (e.g., lower environmental concentrations of biocides for which risk mitigation measures were implemented). In this context the German Federal Environment Agency (Umweltbundesamt) organised in collaboration with the NORMAN network an international workshop in Berlin in June 2015. The discussions focused especially on compartment-specific monitoring approaches and covered aspects such as prioritisation, sampling strategies, measurements and databases. More than 70 workshop attendees from more than a dozen European countries representing authorities, research institutes and universities, industry and industry associations as well as non-governmental organisations participated in the discussions of 13 oral presentations, 13 posters and three break-out groups. This report documents the workshop discussions and abstracts of the contributions as well as the main conclusions drawn.

Contents

Abbreviations

BAC	benzyldimethylammonium compounds
BPD	EU Biocidal Products Directive 98/8/EC
BPR	EU Biocidal Products Regulation No. 528/2012
CMI	chloromethylisothiazoline
DCOIT	4,5-dichloro-2-octyl-2H-isothiazol-3-one
DEET	N,N-diethyltoluamide
DMSA	N,N-dimethyl-N'-phenylsulfamide
DMST	N,N-dimethyl-N'-p-tolylsulfamide
ESB	Environmental Specimen Bank
LC/MS-MS	liquid chromatography / tandem mass spectrometry coupling
LOQ	limit of quantification
PBT	persistent, bioaccumulative and toxic
PNEC	predicted no-effect concentration
PPP	plant protection product
QAC	quaternary ammonium compounds
SGAR	second generation anticoagulant rodenticides
SPM	suspended particulate matter
PT	biocidal product type (according to EU BPD/BPR)
TP	transformation product
UBA	Umweltbundesamt (German Federal Environment Agency)
WFD	Water Framework Directive (2000/60/EC)
WWTP	wastewater treatment plant

1 Introduction

The European Biocidal Products Directive 98/8/EC (BPD) on placing biocidal products on the market was adopted in 1998 and subsequently transposed into national law by the EU member states. It was replaced by EU Biocidal Products Regulation (BPR) No 528/2012 which has applied since September 1, 2013. About 120 biocidal active substances/product type combinations have already been authorised under the BPD or the BPR (list of approved substances; http://bit.ly/1UEIqgl), but many of the substances are still under assessment (biocide review programme; Regulation (EU) No 1062/2014 on the work programme for the systematic examination of all existing active substances contained in biocidal products). The implementation of BPD and BPR has already caused a change in the use of biocidal active substances in Europe. Some substances have been withdrawn from the market, or will be withdrawn soon as a consequence of non-approval decisions. Additionally, the use of certain biocidal substances will be restricted by risk mitigation measures. On the other hand, environmental levels of other biocides may rise as a result of replacement of non-approved compounds.

Environmental monitoring can help in assessing whether the implementation of the BPR has positive effects on the environmental quality (Are lower concentrations detected in recent years?), whether there is a risk (Are the measured environmental concentrations below the derived PNEC?), and whether the exposure estimations applied for risk assessment are realistic (Are the modelling results consistent with the monitoring data?).

In this context and as a follow-up to the first joint workshop in November 2012, UBA (the German Federal Environment Agency – Umweltbundesamt) took the initiative to organise this international event in collaboration with the NORMAN network, to discuss the role of environmental monitoring in assessing the consequences of the EU biocides regulation, with a specific focus on compartment-specific monitoring strategies. A lot of different entry pathways to the environment exist because of the many different uses of biocides. Dedicated sessions were organised to cover monitoring of biocides in urban environments, in surface waters and in terrestrial ecosystems.

More than 70 workshop attendees from more than a dozen European countries representing authorities, research institutes and universities, industry and industry associations as well as non-governmental organisations participated in the discussions of the 13 presentations, 13 posters and three break-out groups.

Scientific and organising committee

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2 Session reports

2.1 Introductory session

On behalf of the German Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety (BMUB) Ms. Eva Dressler gave the welcome address. She greeted the more than 70 workshop participants and highlighted the importance of monitoring activities for biocides in the context of risk assessment. E. Dressler explained that the focus of the biocides authorisation procedure is on single products and that the overall exposure from different products / different uses seems not to be appropriately covered in risk assessment. Biocides monitoring data could help to support a more comprehensive risk assessment. The EU has set rules for the sustainable use of pesticides to reduce the risks and impacts of pesticide use on people's health and the environment (Directive 2009/128/EC). However, biocides are not explicitly addressed (only plant protection products). To ensure the overall aim of a sustainable use of biocides in Europe, data on the actual environmental burdens from biocides are required. Finally E. Dressler wished the participants of the workshop which was co-organised by UBA and the NORMAN Association, fruitful discussions.

The introduction session was chaired by Ms. Jutta Klasen (UBA). She first introduced Ms. Valeria Dulio, the executive secretary of the NORMAN Association (Verneuil-en-Halatte, FR) which co-organised the workshop. V. Dulio welcomed the workshop participants on behalf of NORMAN and expressed her appreciation of this joint activity with UBA. She first presented the activities of NORMAN in the field of emerging environmental substances with a particular focus on biocides. Since 2005 NORMAN has acted as an independent forum of more than 60 leading organisations, facilitating the exchange of information, debates and research collaboration. NORMAN operates various databases, e.g., the EMPODAT database which hosts 6.5 million monitoring data and covers many European member states. Data are gathered together with obligatory metadata in a standardised, interchangeable format which facilitates exploitation of the data. Monitoring data are a central element of the developed prioritisation scheme specifically designed to deal with ‘problematic’ substances for which knowledge gaps are identified. The NORMAN list of emerging substances contains about 860 compounds, of which about 140 are used as biocides (either formerly used, still under review or already approved; also covers compounds additionally used as plant protection products (PPPs) or under other regulations). Monitoring data are available for 66 biocides, but only 29 biocides can be considered as sufficiently monitored (i.e. data from at least four countries). According to the NORMAN prioritisation scheme for monitoring in surface waters some compounds need control / mitigation measures (e.g., deltamethrin, terbutryn, imidacloprid, carbendazim, triclosan). For other substances with a potential risk of exceedance of the predicted no-effect concentration (PNEC), such as e.g., fenoxycarb and tolylfluanid, further monitoring is required for an assessment. Cyfluthrin and permethrin, for example, were identified as substances for which analytical performance should be improved (target: the limit of quantification (LOQ) should be below the PNEC). A further category covers compounds like N,N-diethyltoluamide (DEET) and propiconazole which appear as already sufficiently monitored, but with no evidence of risk for the ecosystems. DEET, for example, is found at relatively high concentration in water but below the environmental protection thresholds. Overall, a complete assessment was not possible because, although data are available for 70% of the compounds that are also used as PPPs, only 15% of the compounds solely approved as biocides in the EU have monitoring data in the database. Moreover, a large majority of the available monitoring data is still limited to the water matrix. Access to the latest information on emerging pollutants, with an overview of benchmark values on their occurrence across Europe, would certainly be of major importance to risk assessors. V. Dulio concluded her presentation with a call for more active collaboration by member states in the sharing of monitoring data as a cornerstone of effective risk evaluation of chemicals.

For the second talk J. Klasen introduced the keynote speaker Ms. Juliane Hollender from the Swiss Federal Institute of Aquatic Science and Technology (Eawag), Dübendorf (CH). J. Hollender heads the department of environmental chemistry at Eawag and she is also an adjunct professor of environmental chemistry at ETH Zurich (CH). Her topic was the current status of biocide monitoring in surface waters in Switzerland. Results of earlier studies had been presented during the previous biocides monitoring workshop in 2012 (report available at: http://bit.ly/1DNsUdI). First, J. Hollender characterised the exposure pathways of biocides which are released to the aquatic environment through various pathways. The biocidal compounds used in Switzerland are quite similar to those used in the European Union. In a screening of wastewater treatment plants (WWTP) 10 of 15 investigated biocides and 1 of 4 covered biocide transformation products were detected with highly fluctuating concentrations from < LOQ up to µg/L levels. Compounds with high concentration levels were, e.g., carbendazim (20–100 ng/L), DEET (up to 8000 ng/L; highest detected levels near Basel obviously from an industrial source), and triclosan (< 40–500 ng/L). Another study investigated biocides in the leachate from facades and roofs of new buildings during rain events. Compounds detected were terbutryn, carbendazim and mecoprop (not notified as a biocide, used as root inhibitor in bitumen roof sheets, this use is covered by the Plant Protection Products Regulation). In 2012 a field study was conducted to screen for all registered biocides and PPPs in Swiss fresh waters. Sites covered areas with different land uses (urban/agricultural), different types of surface waters, areas with high densities of arable crops as well as catchments with cultivation of special crops. Nine bi-weekly time-proportional samplings were performed using automatic samplers. With this approach 22 biocides were detected above their respective LOQ. However, only two compounds were used solely as biocides (DEET, chloromethylisothiazoline (CMI)). In passive samplers which were exposed in parallel, six non-polar biocides (e.g., pyrethroid insecticides) were detected. With this approach low LOQ could be realised which are required due to the low effect thresholds of pyrethroids. Among the most relevant biocides (high levels, in some cases exceedances of quality standards) in Swiss rivers were isoproturon, diuron, CMI, DEET, cypermethrin, deltamethrin, thiacloprid and carbendazim. Finally J. Hollender reported on the monitoring of hydrophobic biocides in lake sediment which is viewed as integrative for contamination within the respective catchments. Sediment cores may be seen as an archive of the past pollution situation. The sediment core monitoring allowed the temporal pollution pattern to be identified, e.g., for time series of personal care products such as triclosan and triclocarban. In a suspect screening, quarternary ammonium surfactants such as benzylalkyldimethylammonium compounds (BAC) were detected. J. Hollender concluded that in Switzerland in agriculturally influenced water bodies plant protection products are mostly more relevant with regard to concentrations and number of compounds in comparison to biocides. Sediment and WWTP sludge, on the other hand, appear to be sinks for some relevant hydrophobic biocides.

In the following discussion on the first two talks it was asked whether the NORMAN databases are publicly available. V. Dulio explained that all data can be retrieved freely after registration. However, users have to agree to cite NORMAN appropriately as the source. Generally, NORMAN is very interested in collecting further monitoring data, from all matrices, and V. Dulio invited participants to share their monitoring data. One participant asked whether certain compounds may be used as indicators for biocide burdens in the environment. J. Hollender explained that this may be difficult for biocides which have very different properties and are applied for very different purposes.

2.2 Session I - General aspects of biocide monitoring

Topic of this session, also chaired by J. Klasen, were general aspects of biocide monitoring, especially the prioritisation of compounds for monitoring in different compartments. First Mr. Heinz Rüdel (Fraunhofer Institute for Molecular Biology and Applied Ecology (IME), Schmallenberg, DE) presented results from a research project on behalf of UBA in which the prioritisation of biocides for environmental monitoring in Germany was investigated. The main purpose of the intended biocide monitoring is to follow changes of environmental concentrations of biocides induced by regulatory measures, e.g., phase-out after non-approval decisions. The approach relies on the data which are available via the (public or confidential) EU biocide assessment reports and covers biocides that are either in the EU biocides review programme or already approved according to the EU Biocidal Products Regulation (No. 528/2012). Relevant transformation products (TPs) are considered if they are covered in the assessment reports and data are available. Biocides are prioritised in a stepwise approach regarding emission potential, relevance for causing adverse effects, and the probability for the occurrence in environmental media (e.g., water, soil, biota). The assessment is mainly based on the intended use of a compound in certain biocide product types (PTs) and their relevance for environmental media. The scores from each step are multiplied and relevant compounds are prioritised according to the total score. For the compartment-specific prioritisation, filters are set considering the partitioning of compounds in the respective compartment (e.g., based on properties such as persistence, bioaccumulation, sorption). For the interpretation of possible monitoring data it has also to be considered whether the compounds are also applied under other regulations (e.g., as PPPs). To allocate environmental findings to the biocides usage, the focus is primarily on compounds currently not approved as PPPs. For the monitoring in the water phase, for example, the prioritised biocides are 4,5-dichloro-2-octyl-2H-isothiazol-3-one (DCOIT), 1,2-benzisothiazolin-3(2H)-one (BIT), 3-iodo-2-propynyl butyl carbamate (IPBC), dichlofluanid, and tolylfluanid. H. Rüdel reported that a plausibility check revealed that some of the prioritised compounds had already been covered in monitoring studies and that positive findings were reported for some.

In the second talk of the session Mr. Frank Sacher (DVGW-Technologiezentrum Wasser, Karlsruhe, DE) presented a procedure for the prioritisation of biocides from the perspective of the drinking water supply. The study was triggered by reports on the occurrence of PPPs and biocides in drinking water resources in Germany where compounds such as diuron, isoproturon, carbendazim or terbutryn were detected. Also the removal efficiency of these compounds in WWTPs is quite low (< 25%). Another compound of concern from the view of drinking water production is tolylfluanid, from which a transformation product derives (N,N-dimethylsulfamide) that can be converted to carcinogenic N-nitrosodimethylamine (NDMA) during ozonation of raw water for drinking water production. Although tolylfluanid has been banned from use in PPPs it is approved as a wood preservative. The presented prioritisation covered about 250 mainly organic-synthetic compounds which were at the time of the study in the biocide review programme or already approved under the EU BPD. The relevance of the biocides was also assessed on the basis of their use in certain biocidal product types (e.g., very high relevance: PTs 7, 8, 10, 11, 19 and 21). Other prioritisation criteria were the EU classification as a high production volume chemical and the solubility and mobility in water (operationalised as water solubility > 10 mg/L and partition coefficient n-octanol/water as log K_{OW} < 4). Toxicity criteria were not included in the prioritisation approach since, for drinking water generally, contamination with anthropogenic compounds should be prevented. F. Sacher reported that 24 not-readily biodegradable biocides were finally identified that were assessed as potentially relevant for drinking water production. Examples of prioritised biocides are diuron, isoproturon, imidacloprid, thiacloprid, clothianidin, tolylfluanid and dichlofluanid. F. Sacher concluded that the monitoring of prioritised biocides in drinking water resources is important to ensure safe drinking water. Moreover, collecting information on the behaviour of priority biocides during drinking water treatment processes seems to be important.

One topic of the discussion in this session was the potential use of biocides production or consumption volumes for assessing the relevance of exposure in the prioritisation approaches, but this approach seems currently impossible since data on consumption volumes are not available. One suggestion regarding this lack was to include biocides usage in EU statistical surveys. Currently the biocidal product type seems to be a pragmatic proxy for the exposure relevance (was used in both prioritisation approaches presented). However, as commented by one participant, the use of a biocidal active substance in a product type is subject to changes in the authorisation decisions. Thus prioritisation lists need updating if the approval situation changes (e.g., if a non-approval decision for the use of a biocide in a certain product type is taken). H. Rüdel explained that the prioritisation should be updated regularly. The necessary (new) data can be obtained from the EU biocide assessment reports. Another factor to be taken into account is that, because of their use in different products (e.g., as PPP, veterinary pharmaceutical, industrial chemical), many biocides are regulated under parallel regulatory frameworks. For this reason the main focus of the presented studies was on those compounds solely used as biocides. For these compounds environmental findings are clearly allocable to the biocide use. One participant asked why the presented prioritisation schemes yielded different results. H. Rüdel answered that one major difference was that (eco)toxicological effects of biocides (e.g., PNEC, toxicity classification) were assessed in the concept developed for UBA (as in the NORMAN approach presented by V. Dulio), while in the scheme presented by F. Sacher such aspects were not considered. Another participant asked why inorganic biocidal compounds were excluded. H. Rüdel answered that it is difficult to assess biocides such as certain copper salts, for example, because these are also used under other regulations and copper compounds also occur naturally. These aspects make it difficult to assess monitoring findings of these compounds. Moreover, special monitoring may be required for certain inorganic biocides (e.g., for metal nanoparticles). A further question regarded the risk of overlooking substances which are difficult to analyse. F. Sacher confirmed that the risk is quite high. Thus compounds for which there are no data or even no proper analytical methods are available should not be forgotten. This aspect is especially taken into account in the NORMAN approach, where a specific action category has been created to prioritise substances for which analytical performance should be improved. One participant commented that techniques are improving and that high resolution methods may help to this end.

2.3 Session II - Biocide monitoring in urban environments (indirect release via wastewater treatment)

The following presentations covered biocide monitoring in urban environments with a focus on indirect releases via wastewater treatment. Ms. Ann-Kathrin Wluka (EMR RWTH Aachen University, Aachen, DE) reported on the fate of biocides during wastewater treatment. The background of the study was findings of compounds such as triclosan or azole fungicides in various environmental compartments in several countries, e.g. surface waters, sewage and sewage sludge. The investigation covered the biocides triclosan, methyltriclosan (transformation product of triclosan), cybutryne, and the azole fungicides propiconazole, tebuconazole, imazalil, thiabendazole and cyproconazole in WWTP-related matrices (sewage, surface water and sewage sludge). First, a sensitive analytical method was established. Like for any multi-parameter method, there is a compromise to be found regarding sensitivity for the different target compounds. For the set of defined target compounds a gas-chromatography-mass spectrometry (GC/MS) method seemed most appropriate since it also allows a stereoselective analysis of both propiconazole and cyproconazole diastereomers (method details were presented on an accompanying poster, see abstract in section 7.3). Samplings were performed at seven German WWTP of different size in North-Rhine-Westphalia and Bavaria. A.-K. Wluka reported that four azole fungicides could be detected in surface water and sewage but concentrations were generally low (> LOQ, but < PNEC). In sewage sludge samples only cyproconazole was detected (< LOQ up to about 400 ng/g dry weight) while levels of triclosan and the other azole fungicides were < LOQ. A.-K. Wluka summarised that concentrations of most of the investigated biocides obviously were low and only sporadically could contamination be detected at these sampling sites.

In the following presentation Ms. Silvia Lacorte (Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, ES) reported on the occurrence of anticoagulant rodenticides in wastewater and sludge. Rodenticides are widely used in domestic applications and urban infrastructure as well as in agriculture (minor use in comparison to urban applications in the investigated region). In this context the potential risks from diseases transferred by pests to humans have to be outweighed by the risk of the biocides to non-target organisms in the environment. First, a liquid-chromatography-tandem mass spectrometry (LC/MS-MS) method was developed to determine relevant rodenticides in waste-water and sludge, to monitor the presence of rodenticides in WWTPs and in receiving urban and agricultural waters, and to study the presence of rodenticides in sludge. S. Lacorte reported that warfarin was the most ubiquitously detected compound in influent waters. Concentrations in WWTP effluents were lower due to a partial elimination in the WWTPs. Examples of other detected compounds were coumatetralyl, flocoumafen, brodifacoum, bromadiolone and difenacoum at ng/L concentrations. Considering water volumes of each WWTP, emissions to receiving waters were estimated to be in the range of 0.02 to 21.8 g per day. In sludge samples several compounds detected in water were also found at ng/g levels, with the highest levels for brodifacoum. S. Lacorte emphasized that the presence of rodenticides in surface waters may pose a risk to aquatic organisms while the potential use of sludge in agriculture is a potential pathway of rodenticides to the soil environment.

Regarding the presentation of A.-K. Wluka it was commented that it was surprising that no triclosan was detected in WWTP effluents. A.-K. Wluka confirmed that triclosan was not detected above the LOQ but had no explanation for this finding. A lower LOQ may be required which could not be realised in the developed multi-parameter method. Another aspect discussed was the difficulty in gaining the permission of WWTP operators to run monitoring programmes on WWTP emissions. Often permission is only given if data are kept anonymous in reports and publications. On the other hand, some WWTP operators are quite keen to cooperate since such studies may help to identify potential problems.

One question regarded the spectrum of rodenticides detected in the study which also covered substances not approved as biocides in the EU in recent years. S. Lacorte explained that the compounds were suggested by local authorities as possible target compounds during planning of the study. Another question was about the possible presence of rodenticides in surface waters. S. Lacorte explained that water downstream of these WWTPs has not been investigated yet.

2.4 Session III - Biocide monitoring in urban environments (direct release or via stormwater)

The following session, chaired by Ms. Ingrid Nöh (UBA, Dessau-Rosslau, DE), covered the monitoring of direct releases of biocides in urban environments and their presence in stormwater. First. I. Nöh introduced Ms. Marie-Christine Gromaire (Laboratory for Water, Environment, and Urban Systems (LEESU), Ecole des Ponts ParisTech, Marne la Vallée, FR) who gave a presentation on run-off of benzalkonium chloride (a mixture of alkyldimethylbenzylammonium chloride compounds with mainly C12- and C14-chain lengths) from roof treatments. The compounds are frequently used for the do-it-yourself and professional de-mossing of roofs of private homes. Treatments with dosages of 4 to 7 g/m² are on average every 5 years. The study comprised both a laboratory study and an in-situ pilot scale study. The highest levels of benzalkonium compounds were detected immediately after treatment (mg/L range). Traces in the µg/L range were still detectable after one year (about 640 mm rainfall). Also the roof material influenced the retention of benzalkonium compounds. From ceramic tiles lower concentrations and total masses were leached than from concrete tiles. A loss of a large fraction of benzalkonium compounds applied to the tiles identified in mass balance calculations was interpreted as due to biodegradation. Finally, M.-C. Gromaire reported the results of simulations of stormwater concentration ranges of benzalkonium compounds at the level of the catchment, which revealed an annual pattern strongly linked to the treatment periods. High concentration levels were followed by rapid decreases in periods without treatment. However, the model currently has some uncertainty since the variability of treatment practices is not covered appropriately. Modelled values are consistent with measured concentrations. While the model does not differentiate between phases, the measurements revealed that benzalkonium compounds were nearly completely bound to the suspended particulate matter phase.

As next speaker Ms. Nöh introduced Mr. Daniel Wicke (Kompetenzzentrum Wasser, Berlin, DE) who reported on the monitoring of biocides in urban stormwater with respect to catchment-specific differences and city-wide loads. In the project micropollutants in urban stormwater were investigated in Berlin over one year. The study targeted concentration levels in five storm sewers of different catchment types and on peak concentrations in receiving rivers. To extrapolate the results to a city-wide scale, modelling was applied. Each of the selected stormwater sewers represented one predominant city structure type (e.g., areas with new buildings, commercial structures or single-family homes). The study applied volume-proportional samplings during events over up to four hours with manual mixing. At each site, 10 to 17 events were sampled and one composite sample per event was analysed for micropollutants. The results for biocides were also compared to monitoring data from other groups of chemicals. The total set comprised 95 substances, of which 65 were detected. The biocides group (including formerly approved compounds and transformation products of biocides) consisted of 15 compounds of which 12 could be detected (e.g., carbendazim, DEET, isoproturon, tebuconazole, terbutryn). Wet weather concentrations of biocides were up to one order of magnitude higher than dry weather levels. D. Wicke reported that stormwater from areas with old houses contained high levels of building material preservatives such as carbendazim, diuron, and terbutryn (up to µg/L concentrations), while in areas with single family homes terbutryn levels were highest. The findings are probably related to recent renovations of buildings (façade insulation, paints). In urban rivers, concentrations of biocides were up to a factor of 10 higher during wet weather events than in dry weather conditions. In summary, D. Wicke stated that the results proved that stormwater is a relevant source of micropollutants such as biocides in urban streams. This holds particularly true for areas dominated by separate sewer systems. The measured loads of biocides in rain run-off had similar levels to those of, e.g., pharmaceuticals in WWTP effluents.

The following presentation by Ms. Ulla E. Bollmann (Department of Environmental Science, Aarhus University, Roskilde, DK) covered the dynamics of biocide emissions from buildings in a suburban stormwater catchment in Denmark. To protect paints and render for facades from algae or fungi growth, biocides such as terbutryn, carbendazim or isothiazolinones are added to the products. Biocides are mobilised by rainwater and may reach surface waters via stormwater run-off. In the 9-month study, biocide emissions in a small suburban stormwater catchment were characterised with respect to concentrations, mass loads and dynamics. Of the covered area of 21.5 ha, 7 ha were connected to a separated sewer system. In the residential area about 140 single family homes were located (5 % facades with renders/paints, 20 % (painted) wood, 75 % brick). The samplings were performed in a flow-proportional manner applying a high resolution automatic sampler. After solid phase extraction analyses were performed by LC/MS-MS. Median concentrations of the covered biocides ranged from about 1 to 100 ng/L. However, during rain events peak concentrations of up to 1800 ng/L were detected. Terbutryn and carbendazim had the highest levels, while concentrations of other biocides studied, e.g., isoproturon, diuron, benzisothiazolinone, cybutryne, and propiconazole, were one order of magnitude lower. U. Bollmann explained that high biocides levels at the beginning of rain events (first-flush phenomena) were only observed in some selected events. Usually, concentrations were evenly distributed over the rain event. Further evaluations revealed that the biocide mass flows during the events correlated with wind-driven rain, but not with the length or intensity of rainfall. Generally a treatment of stormwater would be useful to reduce biocide emissions to surface waters.

As final speaker of the session on direct releases, I. Nöh welcomed Michael Feibicke (Federal Environment Agency, Berlin, DE) who was invited to report on a study to support exposure prognoses for risk assessment of antifouling biocides. The study was conducted in cooperation with Burkard Watermann of LimnoMar (Hamburg, DE). For the environmental risk assessment of antifouling biocides, monitoring data are mainly used to check the outcome and plausibility of the exposure assessments, which are performed by applying generic scenarios based on models. M. Feibicke explained that the study was designed to support the exposure prognosis for antifouling agents for the 'marina' scenario. Data on marina sizes and structures, number of berths, actual number of boats, size classes of boats, types of hull surfaces, hydrological parameters (e.g., tidal period, tidal height), and water quality parameters (e.g., temperature, salinity, pH, dissolved organic carbon concentration) were collected. The inventory covered German marinas representing at least 80 % of the total stock. Aerial photos, marina guides and nautical maps were used as data sources. The study covered 200,600 mooring berths at 3,090 German marinas. Only 3% of the marinas were in marine water, 26% in brackish waters (including estuaries and the Baltic Sea) and 71% in fresh water. With a median of 120 $m^{2,}$ berth sizes are highest at marine sites. M. Feibicke stressed that there is the need to assess agglomerations of marinas more closely in future. In a second part of the project the monitoring of antifouling biocides was performed in the water of 50 selected marinas. Beside water concentrations, water quality parameters and the actual numbers of boats in the berths were also recorded. Compounds and TPs covered were copper pyrithione, the zineb TP ETU, DCOIT and three of its TPs, dichlofluanid and its TP DMSA, tolylfluanid and its TP DMST, copper, zinc, cybutryne and its TP M1, and one herbicidal biocide (terbutryn). M. Feibicke reported that cybutryne, for example, was detected at 70 % of the marinas and that at five sites concentrations were even above the EU WFD environmental quality standard for the maximum annual concentration of 0.016 µg/L. Sediment may act as a sink for antifoulants but was not investigated in this study. The monitoring data were applied to a model (MAMPEC - Marine Antifoulant Model to Predict Environmental Concentrations) in the final part of the study. According to M. Feibicke, comparing the model-derived prognoses with the monitoring data from real marinas revealed the need for improving the models for non-embanked marinas at brackish and freshwater sites.

On the subject of benzalkonium biocides, a participant was interested in whether roofs/facades really needed cleaning so frequently. M.-C. Gromaire answered that in some cases the cleaning is done for technical reasons, but is mostly done for aesthetic reasons. The demand for such treatments may be reduced by better communication to the public about the possible risks of the applied biocides to the environment. In the discussion the question was raised of how mecoprop is regulated. As monitoring data by J. Hollender from Switzerland, U. Bollmann from Denmark and D. Wicke from Germany confirm, the compound is obviously used in urban areas (i.e. in bitumen sheets for roofs to prevent roof penetration by plant roots). However, it is neither approved as a biocide nor in the EU review programme for existing biocides. The uses are correlated to a PPP approval for this purpose.

2.5 Session IV - Biocide monitoring in the terrestrial environment

The fourth session was chaired by V. Dulio (NORMAN Association) and highlighted biocide monitoring in the terrestrial environment. As first speaker V. Dulio introduced Ms. Anke Geduhn (Julius Kühn-Institut, Münster, DE) who presented results from a study on the occurrence of anticoagulant rodenticides in biota in Germany and their pathway in the food web. The study was funded by UBA and covered several approved anticoagulant rodenticides. Anticoagulants prevent blood clotting and cause the delayed death of rodents so that no bait shyness occurs. Non-target small mammals may ingest bait directly (primary exposure) and disperse substances in the environment, while predators may take up poisoned prey or carrion (secondary exposure) and accumulate the substances in the liver and other tissues. In one part of the study small mammals captured near several livestock farms were monitored. Over a period of two years about 1200 animals were analysed for residues of brodifacoum which was used in baits near the farms. A. Geduhn described how all non-target small mammal species carried rodenticide residues, but in different proportions and concentrations. A decreesing fraction of animals with residues occurred with increasing distance from the baiting area. Regarding the temporal distribution it was found that higher brodifacoum exposures were detected after than during the baiting period. Close to the baiting sites brodifacoum biota concentrations above 1 µg/g could be detected. In a second part of the study A. Geduhn and her colleagues investigated how non-target small mammals influence the exposure risk of predators near livestock farms. To this end about 2400 pellets of barn owls were analysed during the baiting campaigns. The measurements revealed that the secondary exposure risk is especially high through field mice (*Apodemus*) and voles (*Myodes*). The risk to barn owls seemed to be especially high in autumn as seasonal variations in the barn owl diet seem to affect risk (low in summer, when species with lower rodenticides residues levels are taken up). The third part of the study investigated how local parameters drive exposure of predators such as red foxes. About 330 liver samples of red foxes were obtained, mainly from rabies monitoring of several German federal states. In about 60% of the animals, rodenticides were found (mainly second generation anticoagulant rodenticides, SGAR). An evaluation of possible predictive factors showed that both livestock density and the percentage of urban area of a region were good indicators for rodenticide residue occurrence in foxes.

In the second presentation in this session Ms. Katherine H. Langford (Norwegian Institute for Water Research (NIVA), Oslo, NO) reported on the occurrence of SGAR in non-target raptor species in Norway. These rodenticides are derivatives of 4-hydroxycoumarins, are persistent, have low elimination rates and a high acute toxicity. The study relied on archived raptor liver samples. Rodenticides were determined by LC/MS-MS after zinc chloride precipitation for protein removal, double acetonitrile extraction, and a heptane extraction for fat removal. K. Langford explained that generally no SGAR residues were detected in osprey, peregrine falcon or gyrfalcon. Residues were found in golden eagle and eagle owl livers. Regarding the compounds, brodifacoum and bromadiolone were detected in 67% of the samples and difenacoum and flocoumafen in 10%. Difethialone, on the other hand, was not found in any biota sample. In higher populated regions of Norway higher residues in raptors were detected. The detected SGAR levels may be high enough to pose a threat to certain individuals. K. Langford concluded that the past SGAR use in Norway clearly leads to residues in non-target raptor species tissues. However, since the regulation of rodenticides application has changed in the meantime and now rodenticides are only available for professional use, residues may be lower in future.

A question from the audience regarded the possible use of first generation anticoagulant rodenticides in Norway. K. Langford answered that they are no longer used due to resistance issues. In the discussion all participants agreed that rodenticides are in general required to prevent damage to, e.g., food and to control diseases. One attendee reported that changes can be observed in rodent control in Germany following the imposition of restrictions (SGARs applications only for professionals). Beside chemical treatments, electronic devices are now also available to control rodents, an approach that seems to have huge advantages for the food industry. However, for certain applications chemical rodenticides are still needed. Companies are developing new substances which may also have new modes of action. Another question raised was whether there is a network for the collection of monitoring data of rodenticides in non-target organisms. One participant mentioned the EURAPMON network (www.eurapmon.net), which gathers metadata on raptor monitoring programmes in Europe. There had already been contact with NORMAN with the offer to host the monitoring data in the NORMAN database.

3 Summary of break-out group discussions

3.1 Introduction to break-out groups

As an introduction to the break-out group discussions on monitoring strategies for biocides H. Rüdel (Fraunhofer IME) presented a proposal on how to implement compartment-specific biocide monitoring taking into account existing monitoring programmes. The talk was based on the results of a project run for UBA. A major aim of biocides monitoring is to follow changes in environmental concentrations of biocides as a consequence of the implementation of the BPR (e.g., decreasing environmental levels of substances for which risk mitigation measures were implemented). Monitoring can inform risk assessors on temporal and spatial trends and allows a check on whether biocide concentrations are above the derived no-effect levels (e.g., PNEC, environmental quality standards). As a consequence of the scarcity of data UBA funded the development of a comprehensive monitoring concept for biocides. Its main purpose is to achieve a better coverage of biocides in existing monitoring programmes. Generally, the proposed monitoring activities should be organised in a stepwise approach, e.g., starting with research projects or screening studies, followed by surveys in selected regions, leading to the inclusion of relevant biocides in routine monitoring programmes. With these aims in mind, H. Rüdel described case studies showing how such biocides monitoring could be done. The first case study regarded an approach for monitoring of raptors in Germany. Rodenticides such as SGAR are (potentially) persistent, bioaccumulative and toxic (PBT). Their take-up with prey may cause secondary poisoning of predators. As a first step a survey with samples from an opportunistic biota monitoring of raptors found dead is suggested. Since appropriate samples are available in a specimen bank for certain regions of Germany, retrospective monitoring would be possible. A second case study covered the monitoring of suspended particulate matter (SPM) and sediment. Both matrices bind both polar and non-polar compounds by different mechanisms. Polar compounds are not completely bound to SPM, but it can be assumed that the bound fraction at a certain site is fairly constant over time. This assumption makes the retrospective monitoring of SPM or sediments especially interesting (e.g., to evaluate the success of risk mitigation measures). Since the German Environmental Specimen Bank (ESB) programme has been archiving SPM samples for about a decade, even retrospective studies can be easily made. Examples of detected compounds in SPM/sediments are azole fungicides and cybutryne (see poster by Pohl et al., abstract in section 7.5), triclosan (PT 1) and several quaternary ammonium compounds (QAC). As a third example H. Rüdel described an approach to include more relevant biocides in monitoring programmes of the water phase of surface waters. Since compliance monitoring is required by the WFD and daughter directives (2008/105/EC, 2013/39/EU), programmes exist in all EU member states. Some biocides (cybutryne, cypermethrin, diuron, isoproturon and terbutryn) are already covered by monitoring obligations of the WFD (Directive 2013/39/EU). Examples of biocides (without PPP approval in Germany) detected in the water phase are triclocarban (EU non-approval decision, phase-out 2009), triclosan (PT 1; until 2015 also authorised for PT 2, 7, 9) and its transformation product methyl-triclosan, cybutryne (PT 21, until 2011 also authorised for PT 7, 9, 10), diuron (PT 7, 10). H. Rüdel emphasised that for better coverage of biocides in surface water monitoring, cooperation is recommended with the German federal states which operate the WFD monitoring. Generally, proposals to include additional biocides in existing monitoring should be supported by basic information on the respective compounds, e.g., use pattern, estimated annual consumption, important properties, data on effect concentrations in the respective compartment (e.g., PNEC for freshwater or soil organisms), and information on analytical methods available for the risk assessment.

3.2 Summary of break-out group (A) - Monitoring of biocides in urban environments (indirect release via wastewater treatment)

Facilitator: Manfred Sengl / LfU Bayern, Augsburg (DE)

Rapporteur: Jan Schwarzbauer / EMR RWTH, Aachen (DE)

The topic discussed in break-out group A covered aspects of biocide monitoring in urban environments with a special focus on effluents from wastewater treatment plants. In detail four different main questions have been handled. These four topics and the main statements and ideas discussed and agreed on in the break-out group are summarised here:

Are the monitoring approaches recommended for the environmental compartments appropriate / useful to receive information about biocides?

Generally, the proposed strategy and procedure for biocide monitoring has been evaluated as an efficient approach, but two aspects need to be optimised or modified. Firstly, the prioritisation step should be handled as flexibly as possible to get the opportunity to react sufficiently to changing conditions. Hence, a more continuous procedure is recommended for selection of biocides relevant for monitoring measures. Periodic re-evaluation and the possibility also to include 'candidates' are needed. In general, the group pointed to an expanded spectrum of analytes, e.g., by lowering the criteria for compounds to be included in the monitoring list. It might be better to analyse too much than too few biocides.

Secondly, the implementation of a 'watch-list' approach is recommended to allow testing of suspected biocides. After an appropriate time period it can be decided to include or to reject these candidates from the monitoring list. Furthermore, the group also emphasised the necessity to initiate complementary screening projects to expand continuously the knowledge of the quality and quantity of biocide emissions. These results should be introduced into current monitoring approaches on a short time scale.

During the discussion it was suggested that, as well as concentrations, biocide loads should also be considered in monitoring programmes. This would allow a more detailed insight into their emission characteristics.

Lastly, the discussion about appropriate prioritisation revealed clearly that information on biocide production volumes and/or application rates are essential key parameters. However, these data are not available so far and, consequently a need for action to get such information is obvious. Alternatively, tools for a reliable estimation of these parameters should be developed.

Biocides are often also used as plant protection products, pharmaceuticals and/or industrial chemical. Are there any further ideas on how differentiation may be achieved regarding the various uses of (active) substances in different application fields?

This aspect was seen as one of the most problematic issues related to biocide monitoring. A very thorough interpretation is required on the basis of specific and indicative substances. Here, those biocides that are exclusively used in urban areas or have very restricted applications can take over a distinctive role, since they can act as key parameters for differentiating the emissions of less specific compounds by complementary quantitative interpretation. An alternative approach would be the additional analyses of indicative by-products known in technical biocide formulations. The complementary occurrence of such indicators would probably also be useful to verify biocide applications. Lastly, knowledge about biocide application of active substances can be obtained by source monitoring projects in the urban environment. This can be done only as separate and individual actions and can just add information to monitoring programmes.

To get the whole picture of the entry of a specific substance to the environment, a combination of monitoring in different compartments may be useful. Which combination would you recommend to receive the maximum information in return for as little investment of time and resources as possible?

The group agreed strongly on the two types of compartments that need to be included in monitoring measures. Firstly, sewage water represents an important sample material comprising influents and effluents of sewage treatment plants. Secondly, surface water should be sampled. River water sampling should be performed upstream and downstream of urban areas for comparison.

With respect to the analytical procedure it is recommended to analyse unfiltered water samples (including suspended particulate matter, SPM) to consider also emissions of biocides associated with particles in the water body.

Other sample materials may be analysed sporadically. These may include aquatic biota (in particular for estimating time trends). Here the German Environmental Specimen Bank can act as a cooperation partner. Also sewage sludge could be subjected to biocide measurements to follow the particle-associated emission potential.

Do you know of further relevant monitoring programmes in Europe which may be used for monitoring biocides, especially for WWTP effluents/influents?

Within the group, knowledge of further monitoring programmes was very limited. Monitoring activities related to the EU WFD seem to be the most relevant base. However, this is obviously not sufficient.

Further aspects

Some further remarks and recommendations were also discussed. Once again the essential need for having data on production values and application rates was emphasised. It was suggested that a statement on this should be sent to the European Commission e.g. by NORMAN or as result of this workshop. In this context, the value of the NORMAN network in particular for knowledge transfer from research projects to authorities was highlighted. Here, the group identified a high potential for optimised exchange between science and stakeholders.

Furthermore, the development of appropriate analytical methods is still needed. Finally, it was recommended that transformation products should be considered at early stages of investigations (monitoring or screening initiatives). Plenty of information on transformation products is already available, hence their implementation in scientific projects and measurement campaigns should be practicable without too great an effort.

3.3 Summary of break-out group (B) - Monitoring of biocides in urban environments (direct release or via stormwater)

Facilitator/rapporteur: Kai Bester / Aarhus University, Department of Environmental Science, Roskilde (DK) and Fabrizio Botta / INERIS, Verneuil-en-Halatte (FR)

This discussion group consisted of approximately 20 persons. As an introduction K. Bester set out the framework of this break-out group. The goal of the group meeting was to open discussion on a number of key questions of biocide monitoring in stormwater:

Are the monitoring approaches recommended for the environmental compartments appropriate / useful to receive information about biocides?

Are there any further ideas on how differentiation may be achieved regarding the various uses of (active) substances in different application fields?

Which combination of monitoring in different compartments is recommended to receive the maximum information in return for as little investment of time and resources as possible?

Are there any relevant monitoring programmes in Europe which may be used for monitoring biocides?

Is a monitoring approach for rainwater sewers (urban runoff) required?

As to the question of which monitoring approaches could be recommended for stormwater to receive information about biocides, participants highlighted that stormwater is a very dynamic compartment and it is therefore very important to control the flow characteristics. Generally, it is necessary to define all the different processes affecting biocide fate and transport via stormwater. The most important goal of stormwater monitoring seems to be the definition of biocides emission factors. Participants stressed the need to identify markers of biocides and include them in stormwater monitoring (e.g., ammonium as tracer of domestic inputs).

Participants added that today it is difficult to find examples of regular monitoring programmes for stormwater in Europe. Some examples were mentioned of spot monitoring campaigns. They were addressed to a limited number of substances (e.g., triclosan in Denmark in 2012).

It is well-known that several active substances used in biocides formulations are also used as plant protection products, pharmaceuticals, and/or industrial chemicals. Regarding the strategies to differentiate the different uses of (active) substances, participants mentioned the need to take into account the application periods before starting a monitoring programme (i.e. sampling outside PPP application periods). Enantioselectivity was mentioned as a possible way to discriminate sources, which should be included in monitoring strategies. Land cover differences and weather descriptors that control the observed responses should be studied prior to any field action. It appears also that most studies are performed downstream of stormwater sewers in the receiving water. Participants suggest that it would be advantageous to measure biocides directly in the stormwater.

To get the full picture of the input of a specific substance to the environment, a combination of monitoring in different compartments may be useful. Recommendations were given on how to obtain the maximum information in return for as little investment of time and resources as possible. Firstly, an investigation of estimated inputs, mainly based on sales data, seems to be of priority interest before launching any monitoring programmes.

To optimise monitoring programmes, a properly focused choice needs to be made of the sampling locations, sample materials and sampling frequency. With respect to data exploitation, exhaustive information about the sampling conditions (e.g., characteristics of the sampling site, composite or spot sample, frequency of sampling, etc.) should be compiled and made accessible together with the monitoring data. Participants recommended that multiple samples should be taken throughout a storm event in order to incorporate changes in concentration / flow and therefore accurately represent the storm event. Data on hydrology are fundamental and should be acquired at the moment of the stormwater sample collection and compiled together with monitoring data. The relevance of the first flush was highlighted.

As regards analytical aspects, participants agreed that the water phase is often the most appropriate monitoring matrix. However, in some cases suspended particulate matter could also be a relevant matrix (e.g., for monitoring of quaternary ammonium compounds).

Participants also discussed the case of marina compartments. For this specific case, greater collaboration is needed between hydrologists, modellers and chemists. Monitoring should be performed in both water and sediment matrices. Alternative sampling techniques, such as passive sampling, could be a very useful tool to monitor the presence and concentrations of low levels of biocides in the marine environment.

Further aspects

In addition to the discussion of the questions set out above, further outcomes of the break-out group discussion include:

- The need to launch field investigations addressed to biocides in rainwater sewers which could be used as case studies. To this purpose the sampling campaigns should be designed in order to be representative of a significant number of rainfall events. There was agreement that prioritisation of biocidal 'families' is very important and monitoring should be focused on biocides applied for specific uses (e.g., film preservatives, rodenticides, wood preservatives, masonry preservatives, in-can preservatives, polymerised materials preservatives, insecticides).
- Consumption data should be made available and accessible to the scientific community and to water managers. Consumption data should be distinguished from production data.
- It was also discussed who should pay for the environmental monitoring of biocides (companies vs. manufacturers/users).
- Some participants representing the industry sector mentioned that their expertise in analytical methods should be shared with regulators.

One important concluding remark of this break-out session was that monitoring of stormwater is of priority importance for the understanding of biocide sources in urban environments.

3.4 Summary of break-out group (C) - Monitoring of biocides in the terrestrial environment (incl. groundwater)

Facilitator: Valeria Dulio, NORMAN / Verneuil-en-Halatte (FR)

Rapporteur: Heinz Rüdel / Fraunhofer IME, Schmallenberg (DE)

V. Dulio (NORMAN association) welcomed the 20 or so participants of the break-out group. After a short roundtable of the participants the group started to discuss aspects of biocides monitoring in the terrestrial environment. For the preparation of the group a proposal for a monitoring concept was provided. The discussions followed the questions which were also provided at the beginning of the workshop.

The first question regarded the usefulness of the proposed monitoring approach (presented in the preparatory material for the break-out group). It described a procedure for incorporating specific monitoring of biocides into the existing monitoring programmes of the terrestrial environment (soil, terrestrial organisms, groundwater). The proposal was prepared from the view of risk assessors. In this context a list of biocides for each compartment had also been derived. The break-out group participants regarded the proposal in principle as appropriate but commented that certain aspects should be considered additionally.

The most important item seems to be that the purpose of the monitoring has to be clearly defined and communicated. It must be considered before the monitoring is started whether the results are expected to be sufficient to decide on possible measures. One question to be answered by the monitoring could be whether the results are sufficient to support a restriction or even banning of a certain compound. Another question could be whether implemented risk mitigation measures were effective. Risk assessors may also be interested in whether concentrations of certain substitutes are increasing.

It was also recommended by the participants that a stepwise approach should be followed. The first step could be a field exposure experiment for a biocide of concern, followed by a broader monitoring survey. However, in certain cases it could by vice versa: the monitoring may yield information on a chemical which then could be checked in a field exposure experiment.

For the monitoring of terrestrial biota it was stressed that soil monitoring should cover both soil biota and soil at the same time. Generally each monitoring programme requires a statistically sound sampling approach. For the practical implementation of a monitoring programme it was suggested to start with sites with expected contamination. These can often be identified by looking at the exposure pathways. Examples of practices relevant to soil exposure are the application of liquid manure, which may contain insecticides used in stables, or the spreading of sewage sludge which often contains disinfectants, either from household or professional usage.

Given the high number of biocides used, it was agreed that grouping of compounds by biocidal product type would be a useful approach to define biocides with similar exposure pathways. For the planning of a monitoring study it was especially recommended to apply the information available from emission scenario documents for selecting probably exposed sites. Relevant for these aspects are, e.g., soils from sites near areas of biocides usage, such as wood preservation sites or sites with infiltration of rainwater from buildings. In any case sampling sites should be characterised appropriately. Metadata should include, e.g., soil properties, agricultural practices (if relevant) and known pollution.

Another question discussed in the group was how a differentiation may be achieved regarding the various uses of biocidal substances in different application fields (e.g., as plant protection product / pharmaceutical / industrial chemical). The group concluded that an important aspect is the choice of the sampling site, which should be based on exposure pathways. For soil, specific situations seem possible where, by this means, a differentiation could be possible (or at least certain exposures could be excluded). For groundwater, on the other hand, it does not seem possible to relate measured concentrations to specific uses of a compound. Possible pollution at a selected site may be identified by a regional survey. Field experiments may be used to investigate specific exposures (e.g., rodenticide applications).

One of the questions raised in the preparatory information for the break-out group was which compartments may be covered together in a monitoring exercise to receive the maximum possible information on the entry of a specific substance into the environment in return for as little investment of time and resources as possible. In this context the combined monitoring of soil and groundwater was seen as a useful approach. Also, the above mentioned combination of soil and soil biota monitoring seems relevant. Another combination for certain (volatile) biocides would be parallel soil and air monitoring (e.g., for compounds applied by spraying, spray drift and volatilisation may be relevant). In any case emission pathways should be considered properly as well as the physical-chemical properties of target compounds.

Then the group covered the question of whether participants have knowledge of relevant monitoring programmes in Europe, especially for soil and groundwater, in which monitoring of biocides is currently covered or at least could be included in future. It seems that routine soil monitoring programmes currently do not cover current-use biocides. Participants only had knowledge of research studies or surveys linked to specific topics. Generally the situation for terrestrial biocides monitoring is worse than for water. While routine monitoring is implemented for some biocides under the EU WFD, no comparable obligatory monitoring is required by a ‘soil directive’. One participant mentioned that in Germany samples from recent surveys of forest soils and agricultural soils are archived (covering about 1000 sites). The latter soil samples in principle could also be used for biocides monitoring. As a promising approach the use of biota samples gathered from non-chemical monitoring programmes was discussed. Small mammals, e.g., foxes which are available from routinely performed rabies monitoring programmes in European countries, could be a valuable matrix for bioaccumulative compounds (as described in the contribution of A. Geduhn; session IV, section 2.5 and abstract, section 6.11). Generally it was stressed that monitoring initiatives could benefit from better links between programmes focused either on chemical or biological issues.

Another topic of the group discussion was the question of whether a special monitoring approach for slurry/manure would be required. Participants agreed that there is strong demand for getting data on input into soils by these pathways, but a shortage of time meant that specific recommendations regarding such monitoring could not be developed in the group.

A further specific question raised in the preparatory material for the break-out group was whether a monitoring approach for groundwater receiving surface water by infiltration would be required. However, the group discussed more general aspects of groundwater monitoring. Here especially the aspect of transformation products of biocides (e.g., for dichlofluanid) which may be more polar than the parent, seems relevant. Other compounds (e.g., metals or other compounds currently not covered in the set of biocides used for prioritisation) may also be relevant for monitoring. One participant mentioned that formaldehyde may be an issue and recommended to check possible exposures. Another participant noted that groundwater for production of bottled water should not be forgotten. Regions of production may require more intensive monitoring.

V. Dulio thanked all participants for the lively discussion and their input to the break-out group results.

4 Workshop closing remarks

Ms. Petra Greiner (UBA, Dessau-Rosslau, DE) summarised the main conclusions of the workshop:

General aspects

- Biocides can be found in relevant concentrations in the environment; some are known to be used in large amounts. Focus of the authorisation procedure is on single products – but the overall exposure from different products / different uses is not covered appropriately.
- Many single findings prove that the use of biocides can cause environmental burdens. However, only for a minority of biocidal active substances are monitoring data available. NORMAN gathers monitoring data on all relevant biocides since these are on the current list of emerging substances.
- However, currently about 60% of the prioritised biocides are not appropriately covered by monitoring according to the NORMAN EMPODAT database (www.norman-network.net/empodat/). Sufficient monitoring data exist from at least 4 countries for only 21 substances. Only 15 identified substances would fulfil the criteria for WFD priority substances (results obtained using the NORMAN approach).
- Available monitoring data underline the need for an EU directive on the sustainable use of biocides (similar to that for plant protection products).
- To address the lack of data on production and usage volumes, there seems to be a need for additional reporting requirements / legislation (analogously to PPPs, where the regulation concerning statistics on pesticides is applied).
- Often active substances which are also used for other applications (e.g., as PPP or pharmaceuticals) are covered in monitoring studies. For these compounds the environmental findings are often not clearly allocable to a specific source. Thus the first focus for the monitoring of biocides should be either on substances only used as biocides or on urban environments (especially covering winter seasons) in order to allow a clearer allocation of pollution sources.
- Some compounds are difficult to quantify at relevant concentration in environmental compartments: active ingredients such as pyrethroids, for example, have low effect levels (PNECs or environmental quality standards) which are below current routine analytical limits of quantification. Here improvements of analytical methods are urgently required.
- Regarding water monitoring: not only the water phase is important, some compounds may also be monitored in sediments (hydrophobic biocides) or other matrices.
- Monitoring results can contribute to the identification of sources of contaminations (e.g., wastewater treatment plant effluents).
- Most of the criteria used for prioritisation of compounds (e.g. exposure relevance, compound inherent properties, etc.) are in general comparable among the various prioritisation concepts. However, it has to be noticed that eco(toxicity) is not always taken into account as a parameter for prioritisation of substances.
- The use of production volumes for assessing the exposure relevance is currently not possible since no appropriate data are available. However, to this end the biocidal product types may be applied as proxy for the exposure relevance. Specific use patterns in different EU member states may have to be considered.
- The presented compartment-specific prioritisation lists are sensitive to changes of biocides approval or non-approval for different product types since the exposure relevance may increase or decrease (an example was presented for triclosan) as a result of the authorisation decisions.
- Supposed regulated substances (plant protection products) do not disappear. Example: tolylfluanid use as a PPP was banned, but transformation products are still found in water resources for drinking water at similar high concentrations as a consequence of its use as a biocide.

- Stormwater was identified as a relevant matrix for biocides used in different kind of product types.
- Soil and groundwater monitoring data are almost totally absent for biocides.
- Shared monitoring data compilation and cooperation with existing monitoring programmes have to be intensified.

Special aspects, e.g., from biocides monitoring case studies presented during the workshop

- Azole fungicides in wastewater treatment: in seven German WWTPs contamination observed sporadically, mainly in the water phase, less contamination in sewage sludge (only cyproconazole was detected).
- Roof treatment using benzalkonium biocides: apparently a widespread practice (not only in France?), higher loads are observed in the roof runoff immediately after treatment, but, depending on material, also after longer rainfall periods.
- Biocides in urban areas in Denmark: direct emissions via stormwater in suburban areas, levels can exceed WFD environmental quality standards; to be followed up: apparently different footprint from that in other European countries.
- Census on antifouling use: leisure boat activity most important for inland waters in Germany; analytical screening at marinas confirmed cybutryne presence at about 70 % of the sites, even at concentrations above a WFD environmental quality standard. Other antifoulants seem (currently) to be less relevant. Monitoring of antifoulants should also cover sediments.
- Metals being part of certain active ingredients (e.g., copper, silver) seem currently not sufficiently considered; challenges are the essentiality of certain metals for organisms as well as other sources which have to be considered.
- Benefit of some biocidal applications/products (e.g., roof treatment) seems questionable when set against the environmental burdens they cause; general recommendation: information for the public on biocides usage should be improved (e.g., for biocides used in building material).
- New findings: rodenticides as emerging contaminants in the water phase, detection of rodenticides in wastewater and sludge – highest concentration found for brodifacoum. Until now the focus was mainly on the terrestrial compartment where SGAR were found in the food chain (predators) and non-target organisms, including protected species. Monitoring data for these compounds may lead to regulatory decisions (risk mitigation measures, phase-out) and may trigger innovations (e.g., electronic rodent trap systems).

Outlook

- The final report of the project on biocides monitoring funded by UBA will be published early next year and will include the workshop documentation; the documentation will also be available through the NORMAN portal (www.norman-network.net/?q=node/202).
- UBA and NORMAN encourage all participants to share their monitoring data on biocides.
- Information exchange on newly planned and existing monitoring projects and programmes is encouraged. Also, any comment on the presented monitoring concepts is very welcome.

Workshop closure

P. Greiner expressed her thanks to the team from Fraunhofer IME and all partners for their good work, to V. Dulio and the NORMAN network for the fruitful cooperation and the support of the workshop, to Landesvertretung Sachsen-Anhalt for providing the nice venue and the hospitality of the staff, and to all colleagues at UBA for their support of the event. She thanked also all speakers for great oral and poster presentations and all participants for fruitful discussions during the sessions and the break-out group phase.

5 Workshop programme

5.1 Day 1

Introductory session

Chair: Jutta Klasen / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau (DE)

Welcome address by Eva Dressler / Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety (BMUB), Bonn/Berlin (DE)

The NORMAN network - Special view on biocides as emerging substances //
Valeria Dulio / NORMAN, Verneuil-en-Halatte (FR), Peter C. von der Ohe / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau (DE), Jaroslav Slobodnik / Environmental Institute, Kos (SK)

Keynote presentation:
Biocide monitoring in Swiss surface waters // Juliane Hollender / Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf (CH)

Session I – General aspects of biocide monitoring

Chair: Jutta Klasen / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau (DE)

Results from the prioritisation of biocides for environmental monitoring in Germany //
Heinz Rüdel / Fraunhofer IME, Schmallenberg (DE), Stefanie Jäger / Federal Institute for Occupational Safety and Health (BAuA), Dortmund (DE), Ingrid Nöh / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau (DE)

Prioritisation of biocides from the perspective of the drinking water supply //
Frank Sacher, Astrid Thoma, DVGW-Technologiezentrum Wasser, Karlsruhe (DE)

Session II – Biocide monitoring in urban environments (indirect release via wastewater treatment)

Chair: Jutta Klasen / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau (DE)

Fate of Triclosan and azole fungicides during wastewater treatment //
Ann-Kathrin Wluka, Jan Schwarzbauer / EMR RWTH Aachen University, Aachen (DE)

Occurrence, elimination, and risk of anticoagulant rodenticides in wastewater and sludge //
Silvia Lacorte, Cristian Gómez-Canela / Department of Environmental Chemistry, IDAEA-CSIC, 08034 Barcelona (ES)

Session III – Biocide monitoring in urban environments (direct release or via stormwater)

Chair: Ingrid Nöh / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau

Benzalkonium runoff from roofs treated with biocide products //
Marie-Christine Gromaire, Antoine Van de Voorde, Catherine Lorgeoux, Ghassan Chebbo / Université Paris Est, LEESU, Champs sur Marne (FR)

Biocides in urban stormwater - catchment-specific differences and city-wide loads //
Daniel Wicke, Andreas Matzinger, Pascale Rouault / Kompetenzzentrum Wasser, Berlin (DE)

Dynamics of biocide emissions from buildings in a suburban stormwater catchment //
Ulla E. Bollmann, Kai Bester / Aarhus University, Department of Environmental Science, Roskilde (DK)

Antifouling biocides in German marinas - Studies to support exposure prognoses for risk assessment //
Michael Feibicke, Federal Environment Agency (Umweltbundesamt), Berlin (DE),
Burkard Watermann, LimnoMar, Hamburg (DE)

Summary of day 1 / Heinz Rüdel / Fraunhofer IME, Schmallenberg (DE)

5.2 Day 2

Session IV – Biocide monitoring in the terrestrial environment

Chair: Valeria Dulio, NORMAN, Verneuil-en-Halatte (FR)

Residues of anticoagulant rodenticides in biota in Germany: Pathway of anticoagulants in the food-web //
Anke Geduhn, Alexandra Esther, Detlef Schenke, Jens Jacob, Julius Kühn-Institut, Münster/Berlin (DE)

The occurrence of second generation anticoagulant rodenticides in non-target raptor species in Norway //
Katherine H. Langford, Malcolm Reid, Kevin V. Thomas / Norwegian Institute for Water Research (NIVA), Oslo (NO)

Introduction to break-out groups

How to implement a compartment-specific biocide monitoring under consideration of existing monitoring programmes //
Heinz Rüdel / Fraunhofer IME, Schmallenberg (DE), Katja Michaelis, Korinna Pohl / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau (DE)

Parallel break-out groups (topics are based on previous sessions)

(A) Monitoring of biocides in urban environments (indirect release via wastewater treatment) //
facilitator/rapporteur: Manfred Sengl / LfU Bayern, Augsburg (DE) and
Jan Schwarzbauer / EMR RWTH, Aachen (DE)

(B) Monitoring of biocides in urban environments (direct release or via storm-water) //
facilitator/rapporteur: Kai Bester / Aarhus University, Department of Environmental Science, Roskilde (DK) and Fabrizio Botta / INERIS, Verneuil-en-Halatte (FR)

(C) Monitoring of biocides in the terrestrial environment (incl. groundwater) //
facilitator/rapporteur: Valeria Dulio, NORMAN / Verneuil-en-Halatte (FR) and
Heinz Rüdel / Fraunhofer IME, Schmallenberg (DE)

Reports from break-out groups in the plenary and discussion

Chair: Heinz Rüdel / Fraunhofer IME, Schmallenberg (DE)

Conclusions and closure of the workshop

Petra Greiner / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau (DE)

5.3 Poster

1. * Biocides in combined sewer systems: Dry and wet weather occurrence and sources. //
Ulla E. Bollmann, Camilla Tang, Eva Eriksson, Karin Jönsson, Jes Vollertsen, Kai Bester / Aarhus University, Department of Environmental Science, Roskilde, Denmark (DK)
2. Determination of Rodenticides in Fish Samples of the German Environmental Specimen Bank //
Matthias Kotthoff, Heinrich Jürling, Mark Bücking / Fraunhofer IME, Schmallenberg (DE)
3. Authorisation of Anticoagulant Rodenticides in Germany //
Anton Friesen, Barbara Jahn, Anja Kehrer, Eleonora Petersohn, Caroline Riedhammer, Kristina Wege, Stefanie Wieck, Beatrice Schwarz-Schulz, Ingrid Nöh / Federal Environment Agency (UBA), 06844 Dessau-Rosslau (DE)
4. * Triclosan emissions and transformations through wastewater treatment plants //
Kai Bester, Xijuan Chen, Haitham el-Taliawy / Aarhus University, Department of Environmental Science, Roskilde, Denmark (DK), Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang (CN)
5. Determination of triclosan and methyl-triclosan in soil and earthworm samples from sewage sludge-treated agricultural sites //
Suman Kharel, Matthias Kotthoff, Heinz Rüdel / Fraunhofer IME, Schmallenberg (DE)
6. Occurrence of N,N-dimethylsulfamide, the degradation product of the fungicides tolylfluanid and dichlofluanid, in the aquatic environment //
Katherine H. Langford, K. Bæk / Norwegian Institute for Water Research (NIVA), Oslo (NO)
7. Passive samplers as a means to monitor urban biocide emissions //
Tom Gallé, Michael Bayerle, Denis Pittois / Luxembourg Institute of Science and Technology, ERIN Dept. – Pollution control and impact assessment group, Belvaux (LU)
8. * Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measurements //
Ann-Kathrin Wluka, Jan Schwarzbauer / EMR RWTH Aachen University, Aachen (DE)
9. * Transformations of triazole fungicides //
Ulrike Mülow, Petra Lehnik-Habrink, Christian Piechotta / Federal Institute for Materials Research and Testing (BAM), Berlin (DE)
10. * Environmental Monitoring of Biocides – Cybutryne and Azole Fungicides in Suspended Particulate Matter Samples //
Korinna Pohl, Katja Michaelis, Andrea Körner, Ingrid Noeh / Federal Environment Agency (Umweltbundesamt), Dessau-Rosslau / Berlin (DE)
11. * Behaviour of tributyltin under the influence of suspended particulate matter //
Janine Richter, Ina Fettig, Rosemarie Philipp, Christian Piechotta, Norbert Jakubowski, Ulrich Panne / Federal Institute for Materials Research and Testing (BAM), Berlin (DE)
12. * Households as emission source for biocidal active substances in urban environments //
Stefanie Wieck, Oliver Olsson, Klaus Kümmerer / Institute for Sustainable and Environmental Chemistry, Leuphana University, Lüneburg (DE)
13. # Antifouling biocides in German marinas - Studies to support exposure prognoses for risk assessment // Michael Feibicke / Federal Environment Agency (Umweltbundesamt), Berlin (DE), Burkard Watermann / LimnoMar, Hamburg (DE)

* abstract available (section 7). # see abstract of oral presentation by Feibicke and Watermann (section 6.10).

6 Abstracts – oral presentations

6.1 The NORMAN network - Special view on biocides as emerging substances

Valeria Dulio*[1], Peter C. von der Ohe[2], Jaroslav Slobodnik[3]

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2: German Federal Environment Agency (UBA), Dessau-Rosslau, Germany

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In the field of emerging environmental contaminants, the NORMAN network (www.norman-network.net) has been active since 2005 as an independent forum of more than 60 leading organisations, facilitating the exchange of information, debate and research collaboration both at the global level and with the European Commission's in-house science services.

NORMAN promotes the use of innovative monitoring and assessment tools for identifying the substances of emerging concern most in need of future regulation. The network maintains various databases (e.g. EMPODAT) and has developed a prioritisation scheme specifically designed to deal with 'problematic' substances for which knowledge gaps are identified. These tools have been significantly improved in recent years (expansion of EMPODAT database from 1 million to more than 6 million records; a new 'ecotox' module to allow systematic collection of ecotoxicity test data from online databases worldwide, plus existing regulatory EQS/PNEC values).

The NORMAN list of 'frequently discussed' emerging substances contains 862 compounds: among them, 253 are "new" substances which have been added to the previous list from 2013, whereas 100 substances are now labelled as 'former NORMAN' emerging substances. As regards biocides, the list contains 151 active substances of emerging concern that are still in use, under review or formerly used and 12 compounds (e.g., cybutryne, cypermethrin, dichlorvos, etc.) that are still listed for data collection but labelled as 'former NORMAN' compounds.

The NORMAN prioritisation scheme [1] helps to identify some compounds which evidently need control / mitigation measures (e.g., deltamethrin, terbutryn, imidacloprid, carbendazim, triclosan). Moreover, it is possible to cite substances for which additional monitoring data would be needed, such as e.g., fenoxycarb and tolylfluanid with a potential risk of exceedance of the PNEC. Cyfluthrin and permethrin were identified as substances for which analytical performance should be improved (target: achieve LOQ < PNEC) and N,N-diethyltoluamide and propiconazole appear as substances already sufficiently monitored and for which no evidence of risk was identified.

Biocides are active substances emitted into our environment which are definitely to be regarded as substances of emerging concern. EMPODAT confirms that biocides are still insufficiently covered in monitoring programmes: data are available for 70% of the compounds that are also used as plant protection products, but only 15% of the compounds used solely as biocides have monitoring data in the database. Moreover, a large majority of the available monitoring data is still limited to the water matrix. Here, obviously, an even more active collaboration of the member states in monitoring data sharing is needed for effective risk evaluation. Access to the latest information on emerging pollutants, with an overview of benchmark values on their occurrence across Europe would certainly be of a major importance for risk assessors.

Reference

[1] Dulio V, von der Ohe PC (eds.). 2013. NORMAN Prioritisation framework for emerging substances, ISBN: 978-2-9545254-0-2.

6.2 Biocide monitoring in Swiss surface waters

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According to the European legislation, biocides are used for all non-plant protection purposes. Target organisms include algae, bacteria and insects on facades or wood, in cosmetic products, in household products, on boats, on surfaces or even on human bodies. Biocides comprise a wide range of compound classes, chemical structures and physical-chemical properties. As a result, biocides are released to the aquatic environment through various pathways with different temporal dynamics, such as wastewater and rainwater. In addition, several chemicals used as biocides are also applied as plant protection products (PPP) on agricultural fields. Quantitative conclusions on the relative contributions of urban and agricultural sources are difficult as they heavily depend on the application pattern and land use but also on the sewage system, the climatic conditions as well as soil type. Next to urban and agricultural sources, the situation can be further complicated by industrial point sources that might result in concentration peaks in surface water.

To get an overview on the different exposure pathways and the resulting contamination of the aquatic environment in Switzerland, recent studies on the occurrence of biocides in several compartments such as wastewater, surface water and sediment were investigated and will be presented at the workshop. For surface waters, almost all organic synthetic biocides that are registered and used in at least one product in Switzerland, stable in water and do not partition to another compartment were screened in 45 bi-weekly time-proportional samples in 5 medium-size rivers by HPLC coupled to high resolution mass spectrometry [1]. Surprisingly, only two biocides were detected that are exclusively used as biocides but about 20 further compounds that are applied also as PPP. Thus, altogether 22 chemicals registered as biocides were found which is relatively few compared to 102 PPPs in total. Passive sampling with silicone rubber sheets revealed additional occurrence of organophosphates and pyrethroids, both also used as PPP and biocides. Hydrophobic biocides like triclocarban were detected in lake sediments, which act to integrate the contamination within catchments. In conclusion, for agriculturally influenced water bodies, pesticides seem more relevant than biocides with regard to concentrations and compound numbers, but this remains unclear for other compartments like sediment.

Reference

[1] Moschet C., I. Wittmer, J. Simovic, M. Junghans, A. Piazzoli, H. Singer, C. Stamm, C. Leu, J. Hollender. ES&T, 2014, 48: 5423–5432.

6.3 Results from the prioritisation of biocides for environmental monitoring in Germany

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In a project initiated by the German Federal Environment Agency (UBA) a concept for the prioritisation of biocidal substances for an environmental monitoring was conceived. The set of covered biocides included compounds for which (public or confidential) EU biocide assess-ment reports as primary data source were available. However, readily biodegradable compounds (e.g. alcohols) or metal salts were not considered. The covered biocides are either in the EU biocides review programme or already approved according to the EU Biocidal Product Regulation (No. 528/2012). Often also data on potential transformation products (TPs) are given in the assessment reports. In total about 170 compounds including TPs were covered by the prioritisation approach.

The proposed prioritisation scheme consists of three steps. In a first step compounds are evaluated for potential direct or indirect emissions into environmental media (mainly based on the intended use in certain biocide product types and their relevance for environmental media as assessed in a previous research project). Additionally, available information on consumption, operationalised, e.g., as number of registered products with the respective biocide in Germany, is applied. The second step covers the assessment of the potential to cause adverse effects based on data available from the assessment reports (e.g., PNECs). In a last step the relevance of biocides for monitoring in an environmental compartment (e.g., water phase, suspended particulate matter, biota for surface waters) is scored. Depending on the compartment, in this step substance-specific properties relevant for partitioning between compartments, persistence and/or bioaccumulation are considered. Finally, for each compartment a list of prioritised biocides is derived.

The final compartment-specific prioritisation lists are discussed with regard to compiled biocide monitoring data from literature and research reports. In the assessment it has also to be considered whether the compounds are also applied under other regulations (e.g., as plant protection products). In these cases it is often not possible to allocate the environmental findings to a specific usage. Consequently, the evaluation has to focus primarily on compounds solely approved as biocides.

6.4 Prioritisation of biocides from the perspective of the drinking water supply

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Biocidal agents are chemicals that are used in a variety of applications for controlling the effects of harmful organisms. Within a research project biocides have been prioritized from a water supplier's perspective.

During an inventory 249 biocidal agents were identified which by December 2011 were already placed on the market or have been notified for authorization on a European level. These 249 compounds were evaluated with respect to their potential for entering raw water resources used for drinking water production and 24 chemicals were finally selected which are regarded as being of high priority for drinking water suppliers. Criteria for priority-setting were chemical identity, possibility of being released into the aquatic environment during the service life of the biocidal product, production volume, and physical-chemical properties as water solubility, mobility and biodegradability. The priority list contains well-known compounds like diuron and isoproturon which have been in use as active ingredients of pesticides for many years but also relatively new compounds like the neonicotinoids imidacloprid, thiacloprid or clothianidin. Furthermore tolylfluanid and dichlofluanid were put on the priority list to take into account their transformation into N,N-dimethylsulfamide (DMSA). Although tolylfluanid has been banned from use as active agent in pesticides it got authorization for use as wood preservation agent.

For the 24 selected biocidal agents it is recommended to improve the data base with respect to the criteria used for their selection. Furthermore analytical method should be made available to study the occurrence of these compounds in the water cycle. Besides analytical measurements for the priority biocidal agents in environmental samples their behaviour in the environment and especially during drinking water preparation should be studied. Only based on the results of these studies a final assessment of the relevance of biocidal agents for drinking water suppliers will be possible.

6.5 Fate of Triclosan and azole fungicides during wastewater treatment

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Biocides have received increasing attention as emerging contaminants in recent years. Triclosan and azole fungicides have been reported in various environmental compartments [1, 2]. Triclosan has been detected in surface water and sewage water in numerous countries such as Germany [3], USA [4] as well as in Switzerland [5] with concentrations from <LOQ [6] to 16.6 µg/L [4]. Triclosan can be detected in sewage sludge with concentrations from 0.5-15.6 µg/g (dry weight) [3]. Furthermore, azole fungicides can be detected at low ng/L concentrations levels in different matrices [3, 7]. This project examined the fate of triclosan, methyltriclosan (transformation product of triclosan), cybutryne and the azole fungicides propiconazole, tebuconazole, imazalil, thiabendazole and cyproconazole in abiotic matrices of various environmental compartments (sewage water, surface water and sewage sludge) passing through urban wastewater treatment plants (WWTP) for monitoring measurements. The sampling strategy included seven German wastewater treatment plants and their corresponding receiving waters in North-Rhine-Westphalia and Bavaria. On site of each WWTP, samples were obtained from influent, sewage water before biological treatment, sewage sludge and effluent. Four samples were collected from the receiving surface waters, three sampling locations were situated downstream and one upstream of the effluent from WWTP. Details of the optimized analytical method are described in the corresponding poster presentation ('Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measurements'). Concentrations of all target analytes were below the limit of quantification (LOQ) for surface water and sewage water. Since LOQ values are below predicted no effect concentrations (PNEC), obviously there is no significant emission of the selected biocides by WWTP into surface water systems. In sewage sludge samples cyproconazole concentrations between <0.1 and 450 ng/g (dry weight) were detected. Concentration values for triclosan and the other azole fungicides in sewage sludge samples were below LOQ.

References

[1] Bester, K., Scholes, L., Wahlberg, C., McArdell, C. (2008). Sources and mass flows of xenobiotics in urban water cycles - an overview on current knowledge and data gaps water. Water Air Soil Pollut. Focus 8, pp. 407-423.

[2] Chen, Z., Ying, G., Lai, H., Chen, F., Su, H., Liu, Y., et al. (2012). Determination of biocides in different environmental matrices by use of ultra-high-performance liquid chromatography–tandem mass spectrometry. Anal Bioanal Chem DOI 10.1007/s00216-012-6444-2.

[3] Wick, A., Fink, G., Ternes, T. A. (2010). Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography-tandem mass spectometry. Journal of Chromatography A.

[4] McAvoy, D., Schatowitz, B., Jacob, M., Hauk, A., Eckhoff, W. (2002). Measurement of triclosan in wastewater treatment systems. Environmental Toxicology and Chemistry, Vol. 21, No. 7, pp. 1323–1329.

[5] Lindström, A., Buerge, I., Poiger, T., Bergqvist, P., Müller, M., Buser, H. (2002). Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. Environ. Sci. Technol./ 36, p. 2322.

[6] Samsøe-Petersen, L., Winther-Nielsen, M., Madsen, T. (2003). Fate and Effects of Triclosan. DHI Water & Environment Environmental Project No. 861 .

[7] Kahle, M., Buerge, I. J., Hauser, A., Müller, M. D., Poiger, T. (2008). Azole Fungicides: Occurrence and Fate in Wastewarer and Surface Waters. Environ. Sci. Technol.

6.6 Occurrence, elimination, and risk of anticoagulant rodenticides in wastewater and sludge

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Anticoagulant rodenticides (AR) are pest control chemicals used to kill rodents and have emerged as new environmental contaminants due to their widespread use in agriculture, in domestic applications and in urban infrastructures. After use, rodenticides are discharged to sewage grids and enter Wastewater Treatment Plants (WWTPs). If not efficiently removed, WWTPs effluents can be a source of AR to receiving waters and they can affect aquatic organisms and other non-target species. Therefore, the objective of the present study was to (i) develop and validate an analytical methodology based in liquid-chromatography-tandem mass spectrometry for the determination of 11 AR in wastewater and sludge and (ii) to determine the occurrence of AR in influents, effluents and sludge of WWTPs receiving urban and agricultural wastewaters.

Wastewaters and sludge consist in very complex matrices which can affect the determination of rodenticides. Thus, method development consisted in optimizing the ionization and acquisition conditions to obtain good linearity, sensitivity and precision at low concentration levels. Mass spectrometric fragmentation patterns were determined to obtain good identification capabilities. Following, extraction conditions based in miniaturized liquid-liquid extraction and solid phase extraction for waters and ultrasonic extraction for sludge were optimized. Overall, good recoveries were obtained and limits of detection were at the low ng level.

Influent and effluent wastewaters were analysed to determine the treatment efficiency and the loads discharged to surface waters. In addition, sludge was also analysed to evaluate their accumulation potential. Warfarin was the most ubiquitous compound detected in influent waters, and was partially eliminated during the activated sludge treatment and low ng L-1 concentration were found in the effluents. Other detected compounds were coumatetralyl, ferulenol, acenocoumarol, flocoumafen, brodifacoum, bromadiolone and difenacoum at concentrations of 0.86 - 87.0 ng L-1. Considering water volumes of each WWTP, daily emissions were estimated of 0.02 to 21.8 g d-1 and thus, WWTP contribute to the loads of anticoagulants to receiving waters. However, low aquatic toxicity was observed using Daphnia magna as a model aquatic organism. Finally, sludge samples contained all compounds detected in water at ng g-1 level, indicating that sludge used as organic fertilizer can be a source of AR to agricultural soils.

6.7 Benzalkonium runoff from roofs treated with biocide products

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Roof maintenance practices involving the application of biocide products to fight against moss, lichens and algae have become quite widespread. These de-mossing biocides are easily available, both to professionals and to individuals, and the product range sold on the French market is extensive The active substance of these products is benzalkonium chloride, a mixture of alkyl benzyl dimethyl ammonium chlorides with mainly C12 and C14 alkyl chain lengths, which is toxic for the aquatic environment (substance under review for PT10).

On the basis of both an in-situ pilot scale study and laboratory rainfall simulations, the evolution of roof runoff contamination over a one year period following the biocide treatment of roof frames was studied. Results showed a major contamination of roof runoff immediately after treatment (from 5 to 30 mg/L), followed by an exponential decrease. 175 to 375 mm of cumulated rainfall is needed before runoff concentrations become inferior to 280 µg/l (EC50 value for fish). The residual concentration in the runoff water remained above 4 µg/L even after 640 mm of rainfall. The level of benzalkonium leaching depends on the roofing material, with lower concentrations and total mass leached from ceramic tiles than from concrete tiles, and on the state of the tile (new or worn out). Mass balance calculations indicated that a large part of the mass of benzalkonium compounds applied to the tiles was lost, probably due to biodegradation processes.

Based upon bench test results and a survey on roof treatment practices, benzalkonium loads emitted to stormwater were modelled at the scale of an urban watershed. Results showed a significant stormwater contamination, mainly linked to the particulate phase. The annual benzalkonium load of stormwater could be in the order of 1.25 kg/impervious ha/year.

6.8 Biocides in urban stormwater - catchment-specific differences and city-wide loads

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Untreated stormwater runoff can be an important source of pollutants entering urban surface waters through separated sewer systems. Beside ‘classic’ stormwater pollutants (e.g. suspended solids or heavy metals), trace organic substances including biocides, plasticizers, flame retardants and traffic related micropollutants started to come into focus in recent years. Sources of biocides include pesticides applied in green areas (e.g. glyphosate) as well as biocides in building materials such as façade paints or sealing materials (e.g. carbendazim, diuron). To evaluate for the first time city-wide annual loads of stormwater-based micropollutants entering urban surface waters, an event-based, one-year monitoring programme was set up in separate storm sewers in Berlin. Monitoring points were selected in 5 catchments of different urban structures (old building areas <1930, newer building areas >1950, single houses with gardens, roads >7500 vehicles/day and commercial areas) to consider catchment-specific differences. Volume proportional samples (one composite sample per event) are analysed for a comprehensive set of 100 micropollutants determined from literature review as well as standard parameters. A load model is being developed to estimate annual loads for Berlin from results of the different catchment types.

First results of monitoring (~75 samples) show that 66 of the 100 micropollutants were detected in stormwater runoff of the investigated catchment types. Regarding biocides, 15 out of 19 compounds were detected in concentrations (EMC) up to 3.4 µg/L (mecoprop). Further-more, results indicate catchment specific differences. For example, pesticides isoproturon and glyphosate are highest in catchment of one-family houses with gardens (garden application), whereas the biocides carbendazim and diuron are highest in old building area (application in building materials e.g. in exterior paints of renovated houses). First outcomes of the load model show that annual loads of stormwater-based biocides reach values up to 30 kg/year (mecoprop), comparable to sewage-based micropollutant loads. Samples taken in an urban stream confirm the relevance of stormwater as source for micropollutants in receiving surface waters with peak concentrations up to 5.7 µg/L (glyphosate).

All in all, results indicate that stormwater may be a relevant source of biocides and other micropollutants to urban streams, particularly in cities dominated by separate sewer systems.

6.9 Dynamics of biocide emissions from buildings in a suburban stormwater catchment

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Biocides as terbutryn, carbendazim or isothiazolinones are added to paints and render in order to protect the facade surfaces of buildings from algae or fungi growth. However, these biocides can be mobilized if rainwater gets into contact with them. Hence, biocides can be found in stormwater runoff. Within a 9 month study the biocide emissions in a small suburban stormwater catchment were analyzed with respect to concentrations, mass loads and dynamics.

The median concentrations were relatively high (around 1-100 ng L 1) while in peak events concentrations up to 1800 ng L 1 were detected. The concentrations were highest for terbutryn and carbendazim (100 ng L 1), while the concentrations of the other studied biocides, i.e. isoproturon, diuron, iodocarb, N-octylisothiazolinone, benzisothiazolinone, cybutryne, propiconazole, tebuconazole, and mecoprop, were one order of magnitude lower. The emissions of biocides into stormwater turned out to be up to 60 µg event 1 house 1. First flush phenomena have only been observed in some selected events, while usually the concentrations were evenly distributed over the rain event. However, the mass flows during the events correlated with the wind-driven rain, but neither with the length or the intensity of rainfall nor the length of dry period.

6.10 Antifouling biocides in German marinas - Studies to support exposure prognoses for risk assessment

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Monitoring data of chemicals are often used to control specific quality norms or to identify the dispersion of new rising substances in the environment. In the area of environmental risk assessment monitoring data are also extensively documented, but more or less only used to check the outcome and plausibility of the exposure assessment. The exposure assessment itself bases normally on generic scenarios and is to a large extent model driven.

Here, a study is presented, which was designed to support the exposure prognosis in the area of antifouling agents and products specified for leisure boats and the scenario 'marina' (EU regulation 528/2012, PT 21). The project named 'How reliable are exposure prognosis of the EU scenario models for 'marina'?' was funded by the Umweltbundesamt (UFOPLAN FKZ 3711 67 432). It consists of 3 working packages (WP):

1. Nationwide census of the German stock of marinas and berths, their regional distribution, marina specific data, i.e. on size, grade of embankment, and harbour infrastructure, which may contribute to additional releases of antifouling active agents (AF agents).

2. 'Snap shot' screening on 50 selected marinas by single water sampling to identify AF agents actually in use. In addition further water chemical parameters were monitored, relevant for the exposure modelling (e.g. fate of the substance) and supplemental enquiry on-site to improve census data.

3. Exposure modelling (MAMPEC V.2.5) by use of data on real marinas gained from WP 1 und 2 to compare outcome of predicted concentration with analytical data.

The census reveals the overriding importance of leisure boat activity at inland waters (71 % of total stock) on a national scale. On these data a proposal for an emission scenario on inland marinas will be developed. Screening on 50 marinas points out, that Cybutryne was proved on 70 % of the sites, whereas on 5 sites concentrations were even above the EU quality standard of 0.016 µg/L (MAC-EQS). Comparing model derived prognoses with analytical findings on real marinas a need for improvement for non-embanked marinas of brackish and freshwater sites is indicated.

6.11 Residues of anticoagulant rodenticides in biota in Germany: Pathway of anticoagulants in the food-web

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In the past the exposure of many predatory species to anticoagulant rodenticides (AR) was confirmed including evidence for reductions in population density. Nevertheless, underlying detailed pathways of AR transfer from bait to prey to predators are often unknown.

We conducted a field study following residues of brodifacoum (BR) from bait to predators. Liver samples of non-target small mammals were screened by HPLC-MS for residues of BR to quantify primary exposure in a biocidal application setting. Exposure of non-target small mammals to BR was high in the direct surrounding of bait application (15 m) and varied considerably between taxa.

Furthermore, we analysed the barn owls' (*Tyto alba*) diet composition and combined results to predict exposure risk for that species. Risk to barn owls seemed high in autumn and winter, when barn owls increasingly preyed on taxa that regularly carried BR residues. Residue analysis of barn owl pellets, liver samples of barn owl prey and of carcasses of predators were used to verify the expected pathway. AR residues were found in 13% of prey individuals (targets and non-targets) collected from barn owl nests, confirming this exposure pathway. Nevertheless, AR residue rarely occurred in barn owl pellets, perhaps to poor uptake of AR in skin tissue and hair and degradation before analysis, whereas carcasses of predatory birds and owls from a larger regional scale were regularly exposed to ARs.

We identified local factors that drive AR exposure of red foxes (*Vulpes vulpes*) on a regional scale. Livestock density and the percentage of urban area were good indicators for AR exposure in red foxes. Mainly residues of second generation ARs could be detected in fox liver samples.

We could reveal detailed AR pathways from bait to predator. This is important for the development and improvement of risk mitigation strategies. This study was funded by the German Federal Environment Agency grant #371063401.

6.12 The occurrence of second generation anticoagulant rodenticides in non-target raptor species in Norway

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Second generation anticoagulant rodenticides (SGARs) are commonly used for rodent pest control in Norway resulting in the potential exposure of non-target raptor species. In this study the occurrence of flocoumafen, difethialone, difenacoum, bromadiolone and brodifacoum was determined in the livers of five species of raptors found dead in Norway between 2009 and 2011. The SGARs brodifacoum, bromadiolone, difenacoum and flocoumafen were detected in golden eagle (Aquila chrysaetos) and eagle owl (Bubo bubo) livers at a total SGAR concentration of between 11 and 255 ng/g in approximately 70% of the golden eagles and 50% of the eagle owls examined in this study. In the absence of specific golden eagle and eagle owl toxicity thresholds for SGARs, a level of >100 ng/g was used as a potential lethal range, accepting that poisoning may occur below this level. Thirty percent (7/24) of the golden eagle and eagle owl livers contained total SGAR residue levels above this threshold. Further estimation of the potential mortality impact on the sampled raptor populations was not possible.

6.13 How to implement a compartment-specific biocide monitoring under consideration of existing monitoring programmes

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The European Biocidal Product Directive (98/8/EC) and the Biocidal Product Regulation (No. 528/2012) cause changes of the use of biocides and consequently of their environmental concentrations. For biocides included in the list of approved substances levels may increase while decreasing environmental burdens are expected for substances with non-approval decisions or implemented risk mitigation measures. Such consequences may be proven by an environmental monitoring. The data would also allow checking whether the concentrations are above derived no-effect levels. However, in most monitoring programmes biocides are not appropriately covered. Traditionally, e.g., in surface waters mainly plant protection products (partly also approved as biocides), compounds from industrial sources and legacy chemicals are monitored. To this end the German Federal Environment Agency initiated a project which aims to develop a comprehensive monitoring concept for biocides.

Main purpose of this approach is to achieve a better coverage of biocides in existing monitoring programmes. Proposed monitoring activities should be organized in a stepwise approach. Ideally, at first a research project or a screening study should be performed. If the screening confirms the presence of biocides in the selected compartment as a next step a survey in different regions could be conducted. Based on the outcome finally an inclusion in routine monitoring programmes may be recommended.

As a first step, relevant compartments were identified and relevant biocides prioritised. These lists are provided to monitoring authorities. For the better coverage of biocides in surface water monitoring, cooperation with the German federal states which operate the Water Framework Directive monitoring is recommended. To allow also a retrospective following of changes, the utilisation of samples from existing specimen banks is suggested. Archived biota samples (e.g., fish or raptor tissues) may be used to identify trends of non-polar biocides in aquatic and terrestrial compartments. For more polar compounds archived suspended particulate matter (SPM) from rivers may be analysed (examples already available). Special aspects may be investigated in a snapshot monitoring (e.g., antifoulants in marinas). For soil monitoring, cooperation with federal states which operate permanent soil investigation sites is recommended. Here research projects seem most appropriate, for example for investigating biocides on sites with liquid manure or sewage sludge spreading.

7 Abstracts – poster presentations

7.1 Biocides in combined sewer systems: Dry and wet weather occurrence and sources

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Biocides are used in building material to prevent growth of algae and fungi. It is known that the biocides are leached out of the material through contact with wind-driven rain. Hence, these biocides are detectable in stormwater run-off and they can also be detected in combined sewer systems during wet periods with concentrations up to several hundred ng L 1.

During the present study the influent concentrations and loads of these biocides have been analysed in five wastewater treatment plants in Denmark and Sweden. Contrary to the expectations the biocides are present also in dry weather when leaching from façade coatings can be excluded as source. The concentrations were in the same order of magnitude as during dry weather, reaching up to several hundred ng L 1. At one of the treatment plants noteworthy high concentrations of propiconazole have been detected (up to 4.5 µg L 1). Some presumptions about possible sources for the biocides were made based on time resolved (12 x 2 h) sampling. While the mass loads during wet weather were highest when the rain was heaviest the emissions during dry weather followed human activities, meaning highest in morning and evening hours and substantial lower during night. The high concentrations of propiconazole are caused by a point source which is assumed to be inappropriate cleaning of spray equipment for agriculture or gardening. Overall, about 20 - 40% of the total biocide emissions were emitted during dry weather, for propiconazole even 92%.

7.2 Triclosan emissions and transformations through wastewater treatment plants

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Triclosan is used as a bactericide in toothpaste and other hygiene products as well as in textiles. Its production volume in Europe is about 500 t/a and all of that is discharged directly into the wastewater.

Removal of triclosan in conventional wastewater treatment is high (85-95%). 30% of that removal is sorption to sludge while the rest is biodegradation.

Under realistic conditions, Triclosan transformation in sludge include methylation to Triclosan methyl, cleavage of ether bonds to form 2,4-dichlorophenol, and a catechol, oxidation of the aromatic rings to form hydroxy- and bihydroxy-Triclosan as well as Triclosan sulfate.

Taking these compounds in consideration the mass balance of Triclosan can probably be closed. However, even though the transformation products can in principle be degraded in sludge, their half-life is relatively high. Indicating towards emissions of these transformation products.

While most European WWTPs emit similar amounts of Triclosan into the aquatic environment, Sweden has been successful in reaching agreements about the decrease of Triclosan usage and emissions, thus Triclosan cannot be detected in Swedish wastewaters effluents.

7.3 Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measurements

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The objective within this project is to work out and validate a simple multi-parameter method for the analyses of biocides in abiotic matrices of various environmental compartments (sewage water, surface water and sewage sludge) for monitoring measurements. Eight target substances were defined for analysing selected sample sets. The group of target analytes comprised triclosan, methyltriclosan (transformation product of triclosan), cybutryne and the azole fungicides propiconazole, tebuconazole, imazalil, thiabendazole and cyproconazole. Sampling took place in seven German urban wastewater treatment plants (WWTP) and their corresponding receiving waters in North-Rhine-Westphalia and Bavaria. On site of each WWTP, samples were obtained from influent, sewage water before biological treatment, sewage sludge and effluent. Four samples were collected from the receiving surface waters, three sampling locations were situated downstream and one upstream of the effluent from WWTP. Water samples from WWTP and receiving waters were extracted using solid phase extraction (SPE) according to Wick et al. 2010. Sewage sludge samples were extracted by accelerated solvent extraction (ASE) and subsequent fractionation with dichloromethane and methanol by micro column liquid chromatography using silica gel and analysis by gas chromatographic-mass spectrometric methods (GC/MS). The analytical method has been checked for sensitivity by the limit of quantification (LOQ) for GC/MS analyses compared to predicted no effect concentrations (PNEC). For monitoring purposes recovery rates have been determined. Matrix effects have decreased by optimizing the extraction methods and the instrumental settings and conditions.

Reference

[1] Wick, A., Fink, G., & Ternes, T. A. (2010). Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography-tandem mass spectometry. Journal of Chromatography A.

7.4 Transformations of triazole fungicides

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Triazole fungicides are a group of widely used pesticides which were first introduced into the market in the 1970s. Since then, they have become the most important group of organic fungicides with a market share of 18.5 % in Germany in 2013 [1]. Although triazole fungicides are quite regularly observed in wastewater treatment plant (WWTP) influents [2], little is known of the technical and environmental transformation reactions they undergo.

In this study, the behaviour of two triazole fungicides in the environmental compartments soil and water, as well as under technical conditions (WWTP), is to be investigated using model systems. This includes monitoring of fungicide concentration as well as identification of possible transformation products or metabolites. Concerning the environment, degradation by global radiation and bacterial metabolism are to be studied. In terms of technical transformations, ozonation, chlorination, photolysis, and remediation using Fenton processes should be investigated. Methods used encompass GC MS as well as UPLC ESI TOF MS. As far as possible, the toxicity of identified transformation products should be studied.

References

[1] Lebensmittelsicherheit, B. f. V. u., Absatz an Pflanzenschutzmitteln in der Bundesrepublik Deutschland - Ergebnisse der Meldungen gemäß § 64 Pflanzenschutzgesetz für das Jahr 2012. Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, Ed. 2013.

[2] Kahle, M.; Buerge, I. J.; Hauser, A.; Müller, M. D.; Poiger, T., Azole Fungicides: Occurrence and Fate in Wastewater and Surface Waters. Environmental Science & Technology 2008, 42 (19), 7193-7200.

7.5 Environmental Monitoring of Biocides – Cybutryne and Azole Fungicides in Suspended Particulate Matter Samples

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Data is limited in Germany on the applied amounts and emission rates of biocidal active substances with regards to the environment. Furthermore, data from environmental monitoring campaigns which could exclusively be attributed to biocidal uses only is rare. Consequently, the Product authorisation in context of the Biocidal Product Regulation (EU) No. 528/2012 (BPR) has started without any information of the actual situation of biocide emission into the environment. As regulatory authority, we are interested if the consequences of the BPR are already observable (e.g. practicability of risk mitigation measures, exclusion and substitution of substances with very high concern). The substance cybutryne is assumed to be a suspected endocrine disruptor and has been identified as a potential candidate for substitution according to the BPR. The antifouling substance which was used as construction material preservative for façades and insulating material as well was banned for this use in 2011. An increase in use of other material preservative substances (e.g. tebuconazole, propiconazole) was therefore expected. The aim of this study was to investigate the occurrence of biocides cybutryne, propiconazole and tebuconazole retrospectively by analysing suspended particulate matter (SPM) samples of the German Environmental Specimen Bank. Sampling areas are assumed to be impacted by urban environments (e.g. emission of municipal wastewater and storm water), whereas the agricultural influence was rather secondary. All three substances were detected at all sampling sites in the lower µg/kg range with a detection limit of 0.1 µg/kg. From 2006 to 2012 cybutryne decreased significantly at two the sampling sites, but no definite trends could be observed at other sampling sites. In cases of propiconazole and tebuconazole, the amounts extracted from SPM samples decreased only at one sampling site significantly during the observation period. At most sampling sites no significant trend could be observed over time.

This study is part of the Research and Development Project (F&E) aiming the 'Validation of a prioritisation concept for biocides and development of a monitoring programme for biocides in Germany'.

7.6 Behaviour of tributyltin under the influence of suspended particulate matter

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The widespread of organotin compounds (OTC), used for example as pesticides, antifouling coatings and PVC stabilizers, results in an extensive input into the environment. OTC show toxic effects already at trace level. The public focus lies on the toxic and estrogenic effective tributyltin (TBT) and its metabolites. In 2000 the European water framework directive (WFD 2000/06/EC) was remitted to standardize the monitoring of aquatic ecosystems and groundwater within the EU. The WFD aims to improve the quality of environmental waters and their sustainable usage. The claimed limit of quantification for TBT is 0.06 ng L-1 for the whole water body. A sensitive analytical method is required to achieve this demand.

For monitoring ground and surface waters representative samples have to be analysed. Therefore it is important to use a non-filtered water sample including all water body contents like SPM and humic substances. Natural water bodies possess a huge amount of organic matter, which imposes rigorous requirements on the analytical method. The main part of dissolved organic carbon (DOC) in water bodies is related to humic substances respectively humic and fulvic acids. Those are able to complex OTCs and therefore, complicate the quantitative extraction of the analyte. The affinity to adsorb on organic material increases which decreasing number of butylgroups. Besides strong interactions between dissolved and suspended particulate matter (SPM), TBT shows a high potential of adsorption on sediments and soils.

The development of traceable measurement methods for monitoring TBT in different water matrices containing SPM und humic substances is presented. The quantification was realized by isotope dilution mass spectrometry (IDMS). The feasibility for detecting TBT in real water samples at the WFD concentration level will be demonstrated.

Reference

J. Richter et al., Environ Sci Pollut Res 2015, (DOI) 10.1007/s11356-015-4614-4.

7.7 Households as emission source for biocidal active substances in urban environments

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A wide variety of biocidal active substances that fall under the Biocidal Products Regulation (EU) 528/2012 (BPR) are designated for the use in households. It is obvious that they are used in biocidal products like insect repellents or disinfectants but the same substances can also be ingredients of other products. For example, preservatives in personal care products do not fall under the BPR but under the Cosmetic Products Regulation (EC) 1223/2009. The objectives of the work presented here are

(i) to identify the biocidal active substances that can be found in households and

(ii) to show the product categories they are used in.

With this knowledge target-oriented monitoring of biocidal active substances in domestic wastewater can be improved and the origin of the emissions can be identified to enable emission reduction measures at the source.

Face-to-face interviews were conducted in approximately 100 households in a selected study site in Germany to obtain detailed information and data on the different uses of biocidal active substances. Members of private households were interviewed using a standardised questionnaire regarding the use of biocidal products, plant protection products, washing and cleaning agents and personal care products. The products that were present in the households were registered with the help of a bar-code reader. During the interviews emphasis was laid on the use of a wide selection of products that might enter the sewage system to record the biocidal active substances used in other regulatory backgrounds.

Results show that a high variety of biocidal active substances can be found in products present in the households. However, they are not primarily found in biocidal products but in personal care products or washing and cleaning agents. Herewith, the study extends the knowledge on the potential sources of biocidal active substances in domestic wastewater and demonstrates how they distribute over the different regulatory areas.

8 List of participants

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