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Environmental monitoring of biocides in Europe - compartment-specific strategies
Workshop Report (June 25–26, 2015 in Berlin)

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 Some substances have already been withdrawn from the market, or may be withdrawn soon as a consequence of non-approval decisions.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.

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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 stereo-selective 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

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[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.

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[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

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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.

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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

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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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