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Workshop

Environmental monitoring of biocides in Europe - compartment-specific strategies

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Abstracts

Oral presentations

O1 The NORMAN network - Special view on biocides as emerging substances

Valeria Dulio[1], Peter C. von der Ohe[2], Jaroslav Slobodnik[3]*

1: INERIS, 60550 Verneuil-en-Halatte, France / Executive Secretary NORMAN Association
2: German Federal Environment Agency (UBA), Dessau-Rosslau, Germany
3: Environmental Institute, Kos, Slovakia / Chairman NORMAN Association

*Corresponding author e-mail address: valeria.dulio@ineris.fr

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, cypermetryne, 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., deltamethrine, terbutryn, imidaclopride, 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.

O2 **Biocide monitoring in Swiss surface waters**

Juliane Hollender[1,2], Aurea Chiaia[1], Christoph Moschet[1,2], Mathias Ruff[1], Heinz Singer[1], Christian Stamm[1], Irene Wittmer[1]*

1: Eawag, 8600 Dübendorf, Switzerland

2: IBP, USYS, ETH Zürich, 8092 Zürich, Switzerland

*Corresponding author e-mail address: juliane.hollender@eawag.ch

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 PPP's in total. Passive sampling with silicon rubber sheets revealed additional occurrence of organo-phosphates and pyrethroides, 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.

O3 **Results from the prioritisation of biocides for environmental monitoring in Germany**

Heinz Rüdel[1], Stefanie Jäger[2], Ingrid Nöh[3]*

1: Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME), Business area 'Environmental Monitoring', 57392 Schmallenberg, Germany
2: Federal Institute for Occupational Safety and Health (BAuA), 44149 Dortmund, Germany
3: Federal Environment Agency (UBA), 06844 Dessau-Rosslau, Germany

*Corresponding author e-mail address: heinz.ruedel@ime.fraunhofer.de

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 assessment 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.

O4 Prioritisation of biocides from the perspective of the drinking water supply

Frank Sacher[1], Astrid Thoma[1]*

1: DVGW-Technologiezentrum Wasser, 76139 Karlsruhe, Germany

*Corresponding author e-mail address: sacher@tzw.de

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. 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 behavior 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.

O5 Fate of Triclosan and azole fungicides during wastewater treatment

Ann-Kathrin Wluka[1], Jan Schwarzbauer[1]*

1: Energy and Mineral Resources Group (EMR), Institute for Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Aachen, 52056, Germany

*Corresponding author e-mail address: ann-kathrin.wluka@emr.rwth-aachen.de

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.

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O6 Occurrence, elimination, and risk of anticoagulant rodenticides in wastewater and sludge

Silvia Lacorte, Cristian Gómez-Canela

1: Department of Environmental Chemistry, IDAEA-CSIC, 08034 Barcelona, Spain

*Corresponding author e-mail address: slbqam@cid.csic.es

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.

O7 Benzalkonium runoff from roofs treated with biocide products

Marie-Christine Gromaire[1], Antoine Van de Voorde[1], Catherine Lorgeoux[2], Ghassan Chebbo[1]*

1: Université Paris Est, LEESU, ENPC, 6 et 8 av. Blaise Pascal, Cité Descartes, 77455 Champs sur Marne, France

2: G2R UMR-7566 CNRS/Université Henri Poincaré, BP 239, 54506 Vandoeuvre-les-Nancy, France

*Corresponding author e-mail address: gromaire@leesu.enpc.fr

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.

O8 Biocides in urban stormwater - catchment-specific differences and city-wide loads

Daniel Wicke[1], Andreas Matzinger[1], Pascale Rouault[1]*

1: Kompetenzzentrum Wasser Berlin, Cicerostr. 24, 10709 Berlin, Germany

*Corresponding author e-mail address: daniel.wicke@kompetenz-wasser.de

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 program 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). Furthermore, 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.

O9 **Dynamics of biocide emissions from buildings in a suburban stormwater catchment**

Ulla E. Bollmann[1], Kai Bester[1]*

1: Aarhus University, Dep. Environmental Science, 4000 Roskilde, Denmark

*Corresponding author e-mail address: ueb@envs.au.dk

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, cybutryn, 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.

O10 Antifouling biocides in German marinas - Studies to support exposure prognoses for risk assessment

*Michael Feibicke *[1], Burkard Watermann[2]*

1: German Federal Environment Agency (UBA), 12307 Berlin, Germany
2: LimnoMar, 22145 Hamburg, Germany

*Corresponding author e-mail address: michael.feibicke@uba.de

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.a. 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.

O11 Residues of anticoagulant rodenticides in biota in Germany: Pathway of anticoagulants in the food-web

Anke Geduhn[1], Alexandra Esther[1], Detlef Schenke[2], Jens Jacob[1]*

1: Julius Kühn Institute, Federal Research Centre for Cultivated Plants, Institute for Plant Protection in Horticulture and Forests, Vertebrate Research, 48161 Muenster, Germany
2: Julius Kühn Institute, Federal Research Centre for Cultivated Plants, Institute for Ecological Chemistry, Plant Analysis and Stored Product Protection, 14195 Berlin, Germany

*Corresponding author e-mail address: Anke.Geduhn@jki.bund.de

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 analyzed 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.

O12 The occurrence of second generation anticoagulant rodenticides in non-target raptor species in Norway

Katherine H. Langford[1], Malcolm Reid[1], Kevin V. Thomas[1]*

1: Norwegian Institute for Water Research (NIVA), Oslo, Norway

*Corresponding author e-mail address: kla@niva.no

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.

O13 How to implement a compartment-specific biocide monitoring under consideration of existing monitoring programmes

Heinz Rüdel[1], Katja Michaelis[2], Korinna Pohl[2]*

1: Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME), Business area 'Environmental Monitoring', 57392 Schmallenberg, Germany

2: Federal Environment Agency (UBA), 06844 Dessau-Rosslau, Germany

*Corresponding author e-mail address: heinz.ruedel@ime.fraunhofer.de

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., antifoulings 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.

Abstracts

Posters

P1 **Biocides in combined sewer systems: Dry and wet weather occurrence and sources**

Ulla E. Bollmann[1], Camilla Tang[2], Eva Eriksson[2], Karin Jönsson[3], Jes Vollertsen[4], Kai Bester[1]*

1: Aarhus University, Dep. Environmental Science, Roskilde, Denmark
2: Technical University of Denmark, Dep. Environmental Engineering, Kgs. Lyngby, Denmark
3: Lund University, Water and Environmental Engineering, Lund, Sweden
4: Aalborg University, Dep. Civil Engineering, Aalborg, Denmark

*Corresponding author e-mail address: ueb@envs.au.dk

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%.

P4 **Triclosan emissions and transformations through wastewater treatment plants**

Kai Bester[1], Xijuan Chen[2], Haitham el-taliawy[1]

1: Aarhus University, Dep. Environmental Science, Roskilde, Denmark
2: Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, China

*Corresponding author e-mail address: kb@envs.au.dk

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.

P8 Sampling, sample treatment and analyses of selected biocides as candidates for monitoring measurements

Ann-Kathrin Wluka[1], Jan Schwarzbauer[1]*

1: Energy and Mineral Resources Group (EMR), Institute for Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Aachen, 52056, Germany

*Corresponding author e-mail address: ann-kathrin.wluka@emr.rwth-aachen.de

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

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.

P9 **Transformations of triazole fungicides**

Ulrike Mülow[1], Petra Lehnik-Habrink[1], Christian Piechotta[1]*

1: BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Straße 11, 12489 Berlin, Germany

*Corresponding author e-mail address: ulrike.muelow@bam.de

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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P10 Environmental Monitoring of Biocides – Cybutryne and Azole Fungicides in Suspended Particulate Matter Samples

Korinna Pohl[1], Katja Michaelis[1], Andrea Körner[2], Ingrid Noeh[1]*

1: Federal Environment Agency (UBA), IV 1.2 Biocides, 06844 Dessau-Rosslau, Germany
2: Federal Environment Agency (UBA), Environmental Specimen Bank (ESB), 14193 Berlin, Germany

*Corresponding author e-mail address: korinna.pohl@uba.de

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 waste water 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 program for biocides in Germany*".

P11 Behaviour of tributyltin under the influence of suspended particulate matter

Janine Richter[1], Ina Fettig[1], Rosemarie Philipp[1], Christian Piechotta[1], Norbert Jakubowski[1], Ulrich Panne[1]*

1: BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Straße 11, 12489 Berlin, Germany

*Corresponding author e-mail address: janine.richter@bam.de

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 ground water 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 analyzed. 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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P12 Households as emission source for biocidal active substances in urban environments

Stefanie Wieck[1], Oliver Olsson[1], Klaus Kümmerer[1]*

1: Institute for Sustainable and Environmental Chemistry, Leuphana University of Lüneburg, Scharnhorststr. 1, 21335 Lüneburg, Germany

*Corresponding author e-mail address: stefanie.wieck@leuphana.de

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 barcode 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.