Environmental monitoring of biocides in Europe

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from prioritisation to measurements

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WORKSHOP REPORT

Contents

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1. Introduction

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 Some substances have been withdrawn from the market, or will be withdrawn soon as a consequence of non-inclusion decisions.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

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

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

Organising committee

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2. Session reports

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

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

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

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

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

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

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

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

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

Manfred Sengl (Bavarian Environment Agency LfU) presented case studies from the monitoring of selected biocides. He covered results from analysis of triclosan and its metabolite methyltriclosan, cybutryne and biocides which are also used as plant protection products. High levels of cybutryne, for example, were especially found in water samples from yachting harbours at Lake Starnberg (above the proposed EQS of 2.5 ng/L). The long-term monitoring of larger rivers for triclosan revealed slightly decreasing concentrations, while methyltriclosan amounts were constant at a lower level (period

2004-2012). Mr Sengl welcomed proposals for extended biocide monitoring based on a well justified and clearly documented prioritisation process. In the discussion Mr Sengl explained that currently only data for priority substances are reported to the German WFD database operated at the Umweltbundesamt. Some biocide data are thus not included, but some of these additional data have been published in thematic reports.

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

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

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

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

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

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

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

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

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

3. Summary of break-out group discussions

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

Facilitator: Bernd M. Gawlik, Joint Research Centre, Ispra (IT)
Rapporteur: Heinz Rüdel, Fraunhofer IME, Schmallenberg (DE)

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

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

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

From the different aspects to be considered there was agreement that consumption figures for biocidal substances are very important. Unfortunately these data are not readily available. Authorisation agencies may have confidential data for production/

consumption volumes of biocides, but the biocides market is much more diversified than the pesticides market. For pesticides, the market seems more transparent, since registrations are held mainly by large companies. For biocides, on the other hand, a large number of smaller companies is placing products on the market (up to several thousand products with one biocidal active ingredient) and the application areas are much broader as compared to pesticides (large number of product types). It was discussed that in future the “letter of access” procedure may be used to generate consumption volumes: for Annex I biocidal compounds, data owners may grant other manufacturers access to data. During this step an intended production volume could be documented.

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

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

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

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

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

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

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

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

Facilitator: Peter Lepom, Umweltbundesamt (DE)
Rapporteur: Jan Schwarzbauer, RWTH Aachen (DE)

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

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

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

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

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

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

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

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

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

Facilitator: Gerlinde Knetsch, Umweltbundesamt (DE)
Rapporteur: Jaroslav Slobodnik, Environmental Institute (SK)

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

Quality and comparability of the data on biocides:

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

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

Databases:

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

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

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

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

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

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

Communication of the data:

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

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

Data sharing/exchange:

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

4. Workshop closing remarks

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

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

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

5. Workshop programme

Day 1

Welcome address

Petra Greiner, Umweltbundesamt, Dessau-Rosslau (DE)

Introduction

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

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

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

Session I – General aspects of (biocide) monitoring

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

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

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

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

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

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

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

Session II – biocide monitoring in surface waters

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

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

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

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

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

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

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

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

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

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

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

General discussion and summary of day 1

Day 2

Session IV – Introduction to break-out groups

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

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

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

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

Parallel break-out groups

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

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

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

Reports from break-out groups in the plenary and discussion

Chair: Heinz Rüdel, Fraunhofer IME, Schmallenberg (DE), Stefanie Jäger, Umweltbundesamt, Dessau-Rosslau (DE)

Conclusions and closure of the workshop

Stefanie Jäger, Ingrid Nöh, Umweltbundesamt, Dessau-Rosslau (DE)

Poster

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

6. Abstracts – oral presentations

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

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

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

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

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

Valeria Dulio[1], Jaroslav Slobodnik[2]*

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

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

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

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

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

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

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

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

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

(Biocide) monitoring in European legislation – The WFD example

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

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

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

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

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

European Environmental Specimen Banks

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What are environmental specimen banks?

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

How do environmental specimen banks work?

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

How do environmental specimen banks support chemical regulation?

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

What kinds of samples are stored in environmental specimen banks?

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

What environmental specimen banks are there in Europe?

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

What chemicals are analysed?

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

Survey of biocide environmental monitoring data in Germany

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

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

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

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

Proposal for the prioritisation of biocides for environmental monitoring

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

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

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

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

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

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

Monitoring of selected biocides – experiences from Bavaria

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

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

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

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

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

Status of biocide monitoring in North-Rhine Westphalia, Germany

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

Biocides are monitored

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

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

Biocide Monitoring in Switzerland

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

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

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

Status of biocides monitoring in France

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

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

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

Biocides in Façades – State of Knowledge

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

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

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

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

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

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

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

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

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

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

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Prioritization of biocides for monitoring campaigns in Switzerland

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

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

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

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

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

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

Databases and exchange of monitoring data - experiences from NORMAN

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

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

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

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

7. Abstracts – poster presentations

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

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

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

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

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

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

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

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Methyltriclosan (MTCS) is a transformation product of the biocide triclosan (TCS) which is commonly used e.g. in personal care products and textiles. Via waste water TCS reaches freshwaters since its degradation in sewage treatment plants (STP) is not complete. Moreover, a fraction of TCS is transformed to MTCS during the STP process. To study levels of the lipophilic MTCS in aquatic biota, muscle of fish (bream, Abramis brama) archived by the German Environmental Specimen Bank were investigated. Standardized annual homogenate samples were analysed by GC/MS directly (MTCS) or after derivatisation (TCS). Fish originated from 17 different German freshwater sites including the rivers Elbe, Mulde, Saale, Rhine, Saar and Danube. The period covered for MTCS was 1992 - 2008. Since TCS levels were low it was only analysed for the period 1992 - 2003 and 2008 (maximum 69 ng/g TCS in Saar fish in 1998; lipid-based data). TCS and MTCS could not be detected in fish from a reference site (Lake Belau, Northern Germany). However, especially in fish samples from rivers influenced by STP effluents high MTCS were detected (e.g., in Saar bream up to 580 ng/g in 2005). For most sampling sites MTCS concentrations were highest in the period 2002 - 2005. Most time series revealed statistically significant increasing trends of MTCS over a decade until about 2003. However, afterwards levels stayed constant or even decreased at nearly all sites. It is assumed that fish body burdens of MTCS are linked to consumption patterns of TCS. Therefore, the decrease of MTCS is probably a result of a voluntary renunciation of the use of TCS in washing and cleaning agents by the member companies of the German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) as announced in 2001.

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

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

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

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

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

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

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

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

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

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

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1. Introduction

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

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

2. Materials and methods

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

3. Results and discussion

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

A criticism sometimes levelled at the WIIS is that it under-records incidents. This is obviously true as there is no doubt some casualties are not found. But, with more than 32 years of continuous WIIS operation, it would have been apparent if there was a failure to detect a major impact on an important wildlife species. It may be significant that populations of the two species of predatory/scavenging birds most frequently found in WIIS incidents, buzzard and red kite, are currently expanding rapidly in the UK. There is no room for complacency, however, because other studies such as those conducted by the

UK Predatory Bird Monitoring Scheme (PBMS) show that exposure of wildlife to anticoagulants in the UK is widespread [3]. Mitigation is required urgently to reduce this contamination [4]. Schemes such as WIIS and PBMS will be important in monitoring impacts of pesticides as the European Commission's Sustainable Use Directive (SUD) [5] is implemented. Within the SUD, a system of risk indicators is applied so that the benefits of the legislation are apparent in the improved health of man and the environment. Monitoring schemes such as WIIS, clearly offering direct and specific risk indicators, will play an important part.

Figure 1. Ten species most common in WIIS incidents (n = 1791)

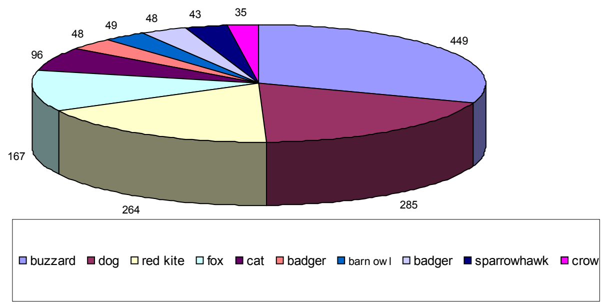
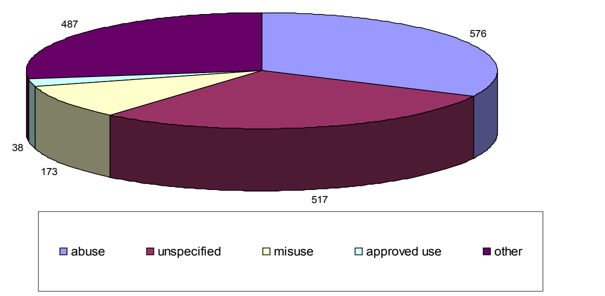


Figure 2. WIIS Incidents by type of use (n = 1791)



4. Conclusions

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

5. References

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Dynamics of biocide emissions from buildings in a suburban stormwater catchment

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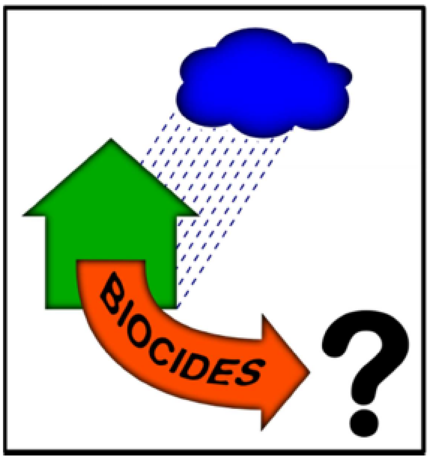
Biocides such as terbutryn and carbendazim are used to protect the façade surfaces of the buildings, would it be painted render or wood. These biocides can be mobilized from the materials if rainwater gets into contact with them. Hence, these biocides will be found in rainwater runoff (stormwater) that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



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

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

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

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

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