TEXTE

114/2017

Are biocide emissions into the environment already at alarming levels?

Recommendations of the German Environment Agency (UBA) for an approach to study the impact of biocides on the environment

For our Environment

Umwelt Bundesamt

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List of abbreviations

AbfKlärV	Sewage Sludge Ordinance
AZM	Pharmaceuticals
BAuA	Federal Institute for Occupational Safety and Health
BCF	Bio-concentration Factor
BDF	Permanent Soil Monitoring Area
BG	Limit of Quantification
BIT	Benzisothiazolinone
BLAC	Federal-State Working Group for Chemical Safety
BLAC ASFV	Federal-State Working Group for Chemical Safety – 'Technical Issues and Implementation' Committee
DBU	German Federal Environmental Foundation
DCOIT	Dichloroctylisothiazolinone
DEET	Diethyltoluamide
DM	Dry matter
DMSA	N'-dimethyl-N-phenyl-sulfamide
DMST	N,N-dimethyl-N'-(4-methylphenyl)-sulfamide
EEA	European Environment Agency
EMPODAT	Database of geo-referenced monitoring and bio-monitoring data on emerging substances
ESB	(German) Environmental Specimen Bank
GrwV	Groundwater Ordinance
JRC	Joint Research Centre
Koc	Distribution coefficient of water-organic substances in soil
KZW	Competence Centre Wasser Berlin
LAWA	Federal-State Working Group for Water
LfU	State Office for the Environment, Bavaria
LfULG	State Office for Environment, Agriculture and Geology, Saxony
LPV/HPV	Low production volume/High production volume
MIT	Methylisothiazolinone
NORMAN	Network of reference laboratories, research centres and related organisations for the monitoring of emerging environmental substances
OGewV	Surface Water Ordinance
PBT	Persistent, bio-accumulative, toxic
PNEC	Predicted no effect concentration
PSM	Plant protection product

PT	Product Type
QAV	Quaternary ammonium compounds
SVHC	Substances of Very High Concern
TP	Transformation product
TrinkwV	Drinking Water Ordinance
UBA	German Environment Agency
UFOPLAN	Environmental Research Plan
UQN	Environmental Quality Standard
WFD	Water Framework Directive
WG	Working Group
WP	Work Package

1 Introduction

The use of biocides can result in alarming impacts on the environment. This has already been confirmed by individual findings of only a few substances, particularly in surface water. This is all the more serious, since the emission of biocides into the environment, particularly from urban areas, will increase sharply in the next two decades, as indicated by recent forecasts from 'SOLUTIONS', a large project funded by the EU Commission (Bunke et al., 2016). However, a comprehensive picture of the actual pollution of the environment with biocides – one that goes beyond such individual findings – is not available, since there is no biocide-oriented, systematic environmental monitoring in Germany to date.

To tackle this problem, the UBA initiated the research project 'Environmental Pollution through Biocides: Development of the Cornerstones of a Monitoring and Measuring Programme for Biocide Emissions into the Environment' (in short: **Environmental Measuring Programme for Biocides**) within the framework of its environmental research plan (UFOPLAN). The aim of the project was to increase the level of knowledge about the environmental impact of biocides by creating the basis for a systematic monitoring program. The project was completed at the beginning of 2016 and the publication of the final report is imminent.

The recommendations given here are largely based on the results of this extensive research project and are particularly intended as a basis and guidance for the future concrete planning of environmental biocide pollution surveys. This report is also intended to enable the federal government to comply with a January 2016 decision of the 'Technical Issues and Implementation' Committee of the Federal-State Working Group for Chemical Safety (BLAC ASFV), which recognises the great importance of a systematic knowledge base on the environmental impact of biocides, and requests that the federal government provide a comprehensive report on the concept for the environmental monitoring of biocides developed by the German Environment Agency. In addition, this report could help to comply with the request that biocides not authorised as pesticides must be increasingly addressed in the monitoring of surface and groundwater. This request is included in the 'Micro-pollutants in Water' report (LAWA 2016), commissioned on behalf of the Federal-State Working Group for Water (LAWA).

As part of the above project, the UBA hosted an international workshop on the environmental monitoring of biocides in 2012, together with NORMAN, the European network of reference laboratories and research centres for the monitoring of new environmental pollutants[1]. This enabled the Agency to gain an overview of[2] existing monitoring activities in the field of biocides in Germany and other European countries. The experts gathered at the workshop unanimously agreed that the flimsy existing (or total lack of) knowledge about biocides made their systematic monitoring in the environment an absolute necessity.

As part of the research project, the UBA consequently had a concept developed, through which biocides can be selected, that are a priority for potential environmental measuring programmes. Initial recommendations were also developed during the project for the concrete implementation of environmental monitoring and measuring programmes for biocides, building on existing information about measuring programmes in Germany and on sampling and analytical procedures (including quality assurance aspects). The clear requirement here was to create data with a minimum of effort.

To ensure that any existing knowledge was used for the monitoring of biocides in Europe, relevant literature was also researched at the same time. It was found that most of the existing biocidal monitoring data originated from surface water monitoring in the context of the Water Framework Directive

1 http://www.norman-network.net

2 The workshop report and the lectures are available to the public at (http://www.norman-network.net/?q=node/99)

(WFD). An evaluation of the NORMAN EMPODAT database and of the EEA surface water database to determine a number of biocides revealed that the ecological effect thresholds (UQN/PNEC) for a number of biocides had been exceeded in surface waters throughout Europe. Frequently recurring examples here were cybutryne, permethrin, triclosan, terbutryn, cyfluthrin and dichlofluanid.

Within the context of this project, the UBA commissioned several experimental studies with the aim of providing an exemplary assessment of the occurrence of possibly relevant biocides in various environmental media. Various azole fungicides, including imazalil and cyproconazole were found in municipal sewage in seven German sewage treatment plants in the corresponding water bodies or in the sewage sludge. Biocidal active substances were also detected in agricultural soils on which sewage sludge had been spread, in the associated earthworm samples (e.g. triclosan) and in suspended matter (e.g. cybutryne, tebuconazole).

One important study encompassed testing procedures for determining active substances in rodenticides (anticoagulant rodenticides) in ESB fish samples. These anticoagulant rodenticides contain SVHCs (substances of very high concern). The inherent properties of these SVHCs make them suitable for the killing of vertebrate animals, but they degrade poorly in the environment (persistent), and they also accumulate in organisms (bio-accumulative). Substances with such a combination of properties are referred to as persistent, bio-accumulative and toxic (PBT). In the assessment of anticoagulant rodenticides in the context of biocidal product authorisation, the UBA identified high environmental risks, especially the risk of secondary poisoning in birds and mammals, and took appropriate risk mitigation measures for the protection of the environment. To date, the focus of these imposed mitigation measures has mainly been on the protection of terrestrial species from poisoning with anticoagulant rodenticides, since residues of the investigated substances have often been found in terrestrial species (e.g. in birds of prey, foxes).

During the current investigation, anticoagulant rodenticides were found for the first time in aquatic biota (in fish samples) in almost all the rivers in Germany, including the Danube, Rhine and Elbe. The concentrations in these fish samples were sometimes so high that a risk to fish-eating predators (e.g. otters) cannot be ruled out.

The protection of the aquatic environment must therefore be increasingly addressed in future assessments of anticoagulant rodenticides. Also included in the picture are the anticoagulant rodenticides which are currently being found in otters (Koivisto et al. 2016.). Within the framework of the 2016 departmental research plan (formerly the environmental research plan), the UBA used these new findings as an opportunity to initiate a follow-up project for an in-depth investigation into the causes of (paths of exposure) and into the extent of the pollution of the aquatic environment by anticoagulant rodenticides. Initial results are expected in 2017; they will be considered in future authorisation procedures for anticoagulant rodenticides and used to adapt risk mitigation measures where necessary.

In 2015, the UBA again hosted an international workshop[3] to ensure that solid and practical recommendations for an approach to the study of environmental pollution with biocides could be derived from the extensive research project, ‘Environmental Measuring Programme for Biocides’. The focus of the discussions between the representatives of authorities, research institutes, universities, industry and non-governmental organisations from more than a dozen European countries was on specific approaches for a biocide monitoring programme in the individual environmental media. The results of the workshop again made it clear that biocides could be found throughout Europe in relevant concentrations, and in the widest possible range of different environmental compartments, such as material preservatives in rainwater drainage and active substances of anti-fouling products in marinas. It was

[3] The workshop report and the presentations are available to the public at www.norman-network.net/?q=node/202.

also reiterated that biocidal active substances were still not being sufficiently addressed in monitoring studies and in routine monitoring programmes.

The UBA has meanwhile developed recommendations for an environmental measuring programme for biocides based on the results of that research project and the two international workshops. These are presented in the following report. New lists of prioritised biocidal active substances and relevant transformation products have also been created, based on an updated data base and the scheme envisaged in the project. A broad, summarised basis has therefore been provided for future, specific UBA surveys of environmental pollution through biocides.

2 Entry paths of biocides into the environment

According to the UBA, the contribution of biocidal products to the environmental impact caused by pesticides is very much underestimated – and this despite the fact that more than 43,000 biocidal products were registered on the German market alone at the beginning of 2017 – and also in spite of the large number of biocidal applications, which also differ greatly depending on the type of product. Examples here are the use of biocides in anti-fouling paints for ships, for the coating of textiles, as disinfectants in hospitals and for combating rats. Biocides thus differ greatly in their complexity of usage compared to plant protection products and pharmaceuticals, although there are striking parallels in terms of application areas, entry paths and product compositions. However, it remains undisputed that the various uses of biocides predictably lead to emissions into the environment.

Due to the substantial number of different usage patterns, biocides reach environmental media on very different entry paths. Biocides are introduced into the environment through direct emissions and so-called indirect entry paths, especially via the municipal sewage system. As a result, all environmental compartments such as surface water, sediments, sea waters, soils, groundwater, atmosphere and organisms are ultimately affected by biocide emissions. Since biocidal active substances are subject to degradation processes in accordance with their individual properties, we must always bear in mind that relevant transformation products can also be emitted into the environment or be created there.

Fig. 1: Relevant entry paths of biocides into the environment

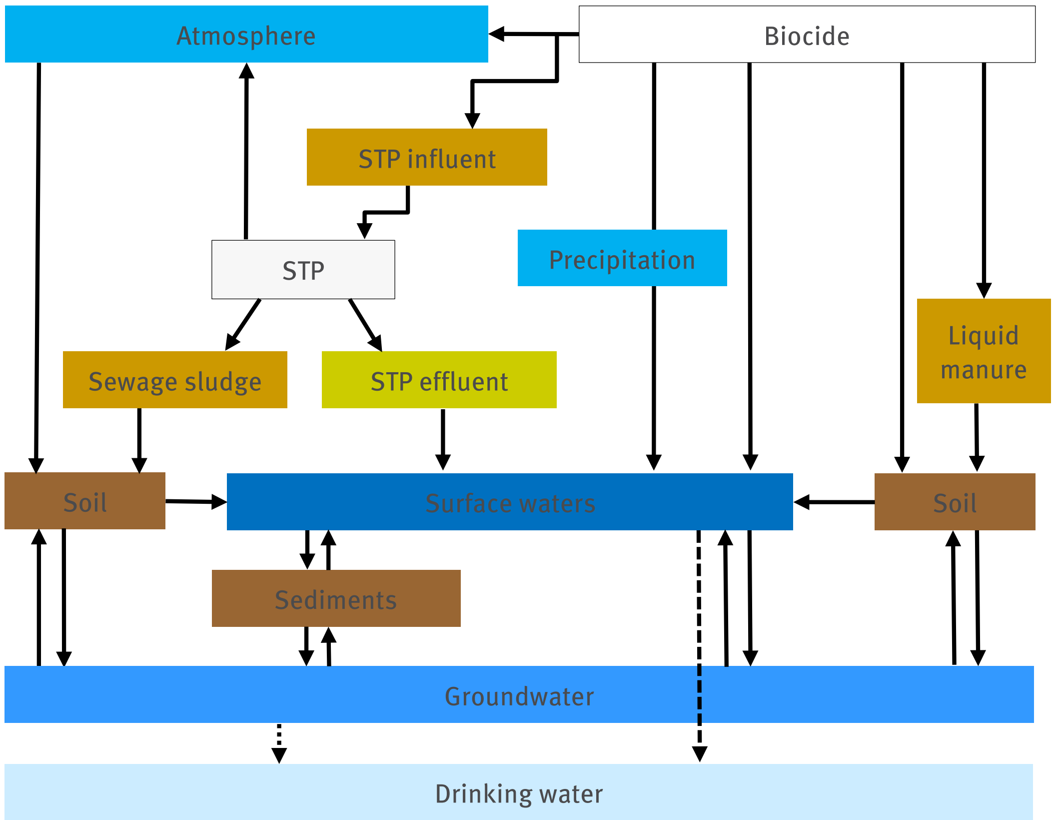

Fig. 1 shows the different entry paths for various applications. In the following text, these are also briefly described using examples. Biocides directly emitted into the atmosphere have been omitted here, since the UBA has rated the impact of these biocides on environmental pollution as low when compared to biocides emitted into the environment through other entry paths.

2.1 Direct entry into surface waters

One prominent example of the direct entry of biocides into surface waters is the release of active substances from anti-fouling ship paints. Anti-fouling coatings contain active substances which are intended to prevent fouling by single-celled organisms, algae, and often hard-shelled animals (such as barnacles and mussels) on ship's hulls. In order to be effective, the active ingredients must slowly dissolve from the coating of paint. Because of this leaching, the paint must be renewed at intervals of roughly one to two years. The substances involved can be highly toxic and can harm local aquatic ecosystems, which include aquatic plants, copepods and algae. The relevance of this entry path is shown by the results of a nationwide active substance screening[4] conducted by the UBA. In the summer of 2013, the active anti-fouling substance cybutryne (irgarol) was tested in 50 sportsboat marinas. In 35 of 50 marinas the concentrations found exceeded the 0.0025 g/L environmental quality standard of the EU Directive 2013/39/EU (Directive relating to priority substances in the field of water policy). As an annual average, this value may not be exceeded. At five marinas, concentrations exceeded the maximum allowable concentration of 0.016 g/L, which normally may not be exceeded even once (UBA 2015a). Wind and waves carry the active anti-fouling substance from the (mostly open) sportsboat marinas to the directly adjacent water bodies of lake and river sections. If the flow rates are greatly reduced here, active anti-fouling substances can also accumulate outside the marinas and occur in such high concentrations that aquatic ecosystems are damaged, as UBA investigations in the Berlin area showed (UBA 2014c). Cybutryne was not authorised as an active biocidal substance due to the unacceptable environmental risks it created (Implementation Decision (EU) 2016/107 on the non-authorisation of the active substance by the European Commission[5]), and due to the wide range of knowledge about its occurrences and the behaviour of the substance in the environment.

The fact that transformation products of active biocidal substances may also not be ignored was also shown in the above-mentioned nationwide study, during which the transformation products of dichlofluanid and tolylfluanid (DMSA and DMST) were detected in 70% and 54% of the samples taken.

A very special use of biocides, one which also results in their direct entry into surface waters is the widespread fight against mosquitoes, where helicopters are also used to spread biocides over large areas. In the first half of 2016, for example, 270 tons of *Bti* granules were dispersed in the mosquito areas along the Rhine River (FAZ, 26.06.2016). *Bti* is the abbreviation for the microorganism *Bacillus thuringiensis israelensis*. Its spores release a toxin in the intestines of e.g. mosquito larvae and this leads to the deaths. The large-scale use of *Bti*, especially on or in nature conservation areas should be regarded critically, however, because scientific literature provides us with evidence of indirect effects in food networks (so an impact on biodiversity cannot be ruled out).

2.2 Direct entry into waters via rainwater drainage

In urban areas where a separate sewer system is present, various protective substances are washed out with the rainwater and subsequently introduced directly into the connected water bodies. These substances may be biocides applied to wood which is exposed to weathering, for example, or biocides applied to plasters or paints to protect façades against algae and fungal attack or to make roofing more durable for outdoor use. Treatment is not usually carried out before the rainwater is discharged into the surface water; in some cases, the rainwater is only stored for a certain time in rainwater collecting basins. According to the UBA, the entry of biocides into surface waters in this way – and in significant quantities – has often been underestimated to date. In most of the developed or areally sealed land

[4] Final report on the research project: http://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_68_2015_sicherung_der_verlaesslichkeit_der_antifouling_0.pdf.

[5] http://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=CELEX:32016D0107&from=EN

zones in Germany a large part of the rainwater drains into the sewer systems. The proportion of separation systems in the public sewer systems in Germany is around 40% (UBA 2005), but there are great regional differences between the respective proportions of the mixing and separation systems, resulting in the clear predomination of the separation system in entire regions. In addition, more and more biocides are being used on thermally-insulated compact façades and on the façades of refurbished buildings, although their use does not lead to increased user satisfaction, according to a study published by the UBA in 2016 (UBA 2016b). The active biocidal substances concerned are known to be persistent and toxic and are very often well-known active substances used in plant protection products. Several of these are no longer authorised by phytosanitary legislation, e.g. terbutryn.

The relevance of this entry path is reflected in the recently-published research project 'Relevance of organic trace substances in Berlin rainwater drainage' by the Competence Centre Wasser Berlin. The rainwater runoffs of five rainwater sewers in Berlin were examined for organic substances (including 15 active biocidal substances) (Wicke et al., 2015). Concentrations of carbendazim, diuron and terbutryn were found to be above the environmental quality standard (annual average) for surface waters or above the aquatic threshold values. Since (at least) carbendazim and terbutryn may no longer be used for plant protection, these substances can only have come from biocidal uses. In the river Panke, a significant increase in the concentrations of the above biocides was also observed during rainy weather, and this illustrates the relevance of rainwater drainage as a source of the entry of biocides into water bodies. A city-wide, annual calculation of biocidal loads in rainwater showed that the levels (up to 30 kg per year) are comparable to those of pharmaceuticals, which are introduced into water bodies via sewage treatment plants.

2.3 Direct entry into soils

The direct introduction of biocides into soils takes place through the runoff of rainwater containing substances from roof and façade areas or from fences, where the rainwater is not discharged into the sewer system, but seeps away locally. The application of plaster, paints, varnishes, etc., can also result in the direct introduction of biocides into soils, e.g. by drip losses during application. Rodenticides (e.g. vole bait) or insecticides (e.g. pouring products against ants) are either introduced to the soils directly or installed in bait boxes in the ground.

The use of products for controlling the oak processionary moth at the edges of woods near settled areas, on public areas such as parks, playgrounds and kindergartens or on avenues can be regarded as a special biocidal application. In this case a drift that cannot be prevented leads to direct introduction into the surrounding soils and possibly also into adjacent waters. To date, the UBA has no knowledge of the extent of soil pollution caused by this drift; however, it is assumed that such biocide usage, which can be very intensive at times, is a cause for local concern.

2.4 Indirect entry into waters

A substantial proportion of biocides enter the environment via so-called indirect introduction – indirect, because these substances only reach water bodies or soils via an intermediate step. In the case of water, the indirect introductions are mainly carried out via sewage treatment plants. It is known that many biocides from different types of products are introduced into sewage treatment plants. Disinfectants are prominent here, but protective products for fibres and leather or insecticides also enter municipal and commercial effluents through the cleaning of the individually-treated products (e.g. treated textiles). Products to ward off e.g. mosquitoes (so-called repellents) are introduced into sewage treatment plants by washing the skin or household surfaces. If rainwater is collected in a combined sewer system and fed to the sewage treatment plant in the urban area in question, the corresponding protection products used on façades and roofs are also found in the waste water.

The extent to which the connected sewage treatment plant is able to eliminate the relevant substances from the wastewater is decisive when it comes to the eventual entry of biocides into water bodies. A distinction is also made here between elimination due to a definitive reduction process (biologically, or by e.g. hydrolysis) and the sorption to the activated sludge. If the active biocidal substance itself or relevant transformation products cannot be eliminated within the sewage treatment plant, they will enter surface water with the STP effluent.

One prominent example here that this entry path can be very relevant is the antibacterial active substance triclosan, which was (among other purposes) tested as a disinfectant for human hygiene. Triclosan enters sewage treatment plants with the wastewater, thanks to the use of products like liquid soaps. The degradation processes in the sewage treatment plant then create the transformation product methyltriclosan, a potential PBT substance. It has been proved that both Triclosan and Methyltriclosan enter the aquatic environment (e.g. Lindström et al. 2002, Bester 2005, Rüdel et al. 2013). There they are very poorly degraded and have a high potential to accumulate in aquatic organisms and consequently in the food chain. Triclosan was not authorised as an active biocidal substance due to the unacceptable environmental risks it created (Implementation Decision (EU) 2016/110 on the non-authorisation of the active substance by the European Commission[6]), also due to the well-known entry paths and the behaviour of both substances in the environment. Triclosan was also listed in the amendment of the Surface Water Ordinance (OGewV 2011) as a river basin specific pollutant, which would be subject to future monitoring in surface waters. For the first time, Germany had to provide an inventory of entries, emissions and losses of priority substances pursuant to Art. 5 of the EU Directive 2008/105/EC (UBA 2016a) in 2013. The material protection products diuron and isoproturon were also included in this inventory. The assessment showed that both substances had to be classified as 'relevant Germany-wide' for surface waters. Since the municipal sewage system is an important entry path for both substances, an assessment of the substance introductions via this entry path was also necessary. The Germany-wide records of municipal sewage treatment plants were therefore estimated for the year 2010 by means of emission factors. The total load level of isoproturon was 234 kg/a, while that of diuron was 467 kg/a. Attempts were also made to calculate path-specific entries for both substances by means of a regionalized path analysis. In the case of isoproturon, diffuse entries such as surface runoff dominate by far, while in the case of diuron, it is assumed that (due to the modelling) it is mainly urban rainwater systems (and municipal sewage treatment plants) that play an important role as entry paths. In the case of both substances, however, it was emphasised that the data situation was generally not satisfactory for the modelling procedure. Reliable analyses (as seasonally-triggered as possible, and on areas as wide as possible) had to be performed on e.g. combined waste water overflows and rainwater sewers of the separate system.

A monitoring project was also initiated as part of the survey (DBU 2014). In a project that lasted for several months, diuron and isoproturon were analysed in influent and effluent samples (or in the sewage sludge) taken from three sewage treatment plants (combined waste water, equivalent to a volume produced by between 44,000 and 500,000 inhabitants); dry and wet weather periods were taken into account. In almost all influent and effluent samples, both substances were found at concentrations that were partially above the valid environmental quality standard – and barely contained in the sewage treatment plants. Both substances were also regularly detected in sewage sludge. A load levels calculation also showed that the average daily levels in rainy weather are significantly higher for both diuron and isoproturon than the dry-weather levels. This supports the assumption that the use of biocides as material preservatives, e.g. on façades, is responsible for the entries of both substances into the environment.

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6 http://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=CELEX:32016D0110&from=EN

The Saxon State Office for Environment, Agriculture and Geology (LfULG) also examined several active biocidal substances and transformation products in municipal sewage treatment plants in Saxony between 2011 and 2012. This project was part of the fifth inventory of effluent emissions in Saxony (LfULG 2014, Engelmann 2016) et al. The aim was to assess the extent to which sewage treatment plant influents were a source of pollution for flowing waters in the case of certain substances. The quality parameters[7] were exceeded in at least 10% of the waste water samples in the case of triclosan, carbendazim, cybutryne, DEET, isoproturon and terbutryn.

During the UBA project, 'Environmental Measuring Programme for Biocides' mentioned above, the influents and effluents of seven sewage treatment plants in Germany were tested for five azole fungicides. All the azole fungicides were detected in the nanogram range in at least one plant. Imazalil, a substance that has a potential disrupting endocrine effect and which is currently being tested throughout the EU, evinced increased concentrations of up to around 800 ng/L in one sewage treatment plant effluent which means that concentrations in the region of the aquatic threshold values (currently 1070 ng/L) were observed.

The Bavarian State Office for Environment (LfU) also carried out surface water tests to measure the amounts of 20 active biocidal substances that are sometimes used in other regulatory areas. The quantities of isoproturon (also used in crop protection) exceeded the environmental quality standard, especially in the autumn and winter months. The findings in the winter months suggest that biocide applications (of preservatives) are responsible for these entries.

2.5 Indirect entry into the soil via sewage sludge

Biocides and relevant transformation products are also eliminated in sewage treatment plants by sorption to sewage sludge. In the above-mentioned UBA project, cyproconazole, for example, was found in four of seven sewage sludge samples. The concentrated amounts of this azole fungicide – which is suspected of being endocrine-disruptive – were at maximum levels of approx. 400 µg/kg calculated on the basis of dry matter (DM). In the case of concentrations of other chemicals (e.g. polychlorinated biphenyls) at this level, the application of sewage sludge to agricultural soils is prohibited pursuant to the Sewage Sludge Ordinance (AbfKlärV, 1992).

If the sewage sludge is treated in the digester, the sorbed substances in the extracted sludge are subjected to anaerobic biodegradation. For some substances, this can lead to a significant decrease in the amount present in the sludge, as was shown, for example, in the case of permethrin (Kupper et al. 2006). If, however, the sorbed active biocidal substances are not anaerobically degraded or liquid sludge is spread (without digester treatment), the biocides are indirectly introduced into the soil of the agricultural land together with the sewage sludge.

The great importance of this entry path was shown by recent findings in samples collected as part of the UBA 'Environmental Measuring Programme for Biocides' project. Samples were taken from soils that had been treated with sewage sludge for two years in Lower Saxony and analysed for the two substances triclosan and methyltriclosan. Even 19 months after the last application of sewage sludge, residues of up to 0.5 µg/kg of triclosan and about 1-2 µg/kg of methyltriclosan (both based on DM) were found in these soil samples. This confirms the assumption that these persistent substances accumulate in the soils.

7 The quality parameter for triclosan is based on a proposed environmental quality standard (UQN-V) of 0.02 µg/L (as of 2012); in the case of carbendazim and DEET, the quality characteristic value corresponds to the test value 0.1 µg/L, while for cybutryne, isoproturon and terbutryn the respective annual average environmental quality standards (UQN) in Appendix 5 of the Surface Waters Ordinance (2011) were used as a basis (UQN cybutryne 0.0025 µg/L, UQN isoproturon 0.3 µg/L and UQN terbutryn 0.065 µg/L).

2.6 Indirect entry in soil and groundwater via liquid manure

According to current knowledge, the indirect entry of biocides into agricultural soil via liquid manure is to be expected, both for disinfectants used for veterinary hygiene and for insecticides used in animal stalls. After the exposure estimates have been carried out as part of the decision on the authorisation of active substances, this will be the case for products containing imidacloprid (insecticide) and cyanamide (disinfectant). After the liquid manure has been spread, rain can carry the biocides or relevant transformation products in question into deeper soil layers and even right down to the groundwater – and this may pose a problem for drinking water. The fact that this entry path can lead to alarming pollution levels of the groundwater is shown by studies conducted in the field of veterinary pharmaceuticals, which also enter the soil via liquid manure, exactly like biocides. One study showed that sulfamethoxazole seeped from a sandy soil (which had been regularly fertilised with liquid manure) into near-surface groundwater (Balzer et al., 2016). The concentrations of veterinary antibiotics were above the groundwater threshold of 0.1 µg/L[8].

2.7 Displacement to other environmental media and accumulation there

The entry of biocides into an environmental compartment is always followed by a displacement of the substances in other environmental media. The extent of this displacement is dependent on the respective substance properties. In the case of entries into surface waters, for example, binding to suspended matter or to sediments takes place. The Environment Agency Austria is currently surveying pollution in harbour waters and the sediments deposited there by active anti-fouling substances (Environment Agency Austria 2015). Cybutryne was the most frequently-detected active substance in the sediment. The measured concentrations even exceeded the 0.18 ug/kg (DM) non-legally binding, sediment-specific quality standard for benthic organisms.[9] Further publications worldwide confirm the displacement of biocides from the water phase into the sediment (e.g. Albanis et al. 2002, Hannachi et al. 2016). Depending on their individual properties, substances from the surface water can also be carried into the bank filtrate, where they could pose a problem for drinking water.

If biocides are introduced into soils through any entry path whatsoever, they can seep into deeper ground layers when it rains, even penetrating down to groundwater level. In the joint research project 'KURAS[10] (Concepts for Urban Rainwater Management and Sewer Systems)' lysimeter studies were carried out with roof drainage water intended for rainwater infiltration. UBA has a partner role in KURAS. The results showed, for example, that the active substance mecoprop (authorised as a plant protection product), which is washed out of bituminous roofing sheets, can still be detected in water after passage through a soil column.

If an accumulation of biocides takes place in organisms, the risk of an undesirable effect in the non-target organism (primary poisoning) is very real, despite a very low environmental concentration. On the other hand, accumulations can also occur in the food chain, and this endangers even more organisms (secondary poisoning). During the course of the UBA research project mentioned above ('Environmental Measuring Programme for Biocides'), tests were carried out on earthworms taken from areas that had been treated with sewage sludge for many years. Triclosan concentrations of around

8 As far as the threshold for plant protection products and biocides is concerned, no legal precautionary limit for pharmaceuticals has been established to date.

9 Cybutryne EQS dossier 2011 (https://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=3&ved=0ahUKEwjelNnj9ODNAhUF8RQKHYmuCFMQFggrMAI&url=https%3A%2F%2Fcircabc.europa.eu%2Fsd%2Fd%2F1eb5aa3b-bf6c-48ca-8ce0-00488a0c2905%2FCybutryne%2520EQS%2520%2520dossier%25202011.pdf&usg=AFQjCNHQ8YuI9pqFiOhC_hIEBOtyoOSxzQ&bvm=bv.126130881,d.d24&cad=rja)

10 http://www.kuras-projekt.de

700 µg/kg DM were found in the worms. Compared with the corresponding concentration in the soil, this value represents an accumulation in earthworms of more than a factor of 1000.

3 Recommended modules to survey the environmental impact of biocides

As explained in Chapter 2, biocides and their transformation products enter into various environmental media by means of different entry paths, depending on the area of application. This means that not every biocide will inevitably be found in relevant concentrations in all environmental media.

Against this background, the UBA suggests that a **modular system** be used to carry out a survey of environmental pollution by biocides. In the opinion of the UBA, each module can be viewed as a stand-alone work package. The work packages are designed in such a way that the level of biocidal pollution via the same entry paths can be acquired. Accordingly, the UBA has used a prioritisation concept (see Chapter 4) to create its own list for each work package, containing proposals for measuring priority active substances and transformation products. The work packages, however, are only outlined in general at this point in time. Chapter 6 contains detailed proposals for the concrete implementation of tests.

An overall picture of the environmental impact of biocides would be obtained if all the proposed work packages were processed. From the perspective of the UBA, this would be the ideal scenario. However, the work packages have been designed in such a way that separate or successive implementations will provide conclusive results in themselves.

In the case of separate or successive processing of individual work packages, the UBA has undertaken a weighting process for the proposed modules. Weighting will ensure that those measurements (which the UBA believes will provide a realistic picture of the environmental impact of biocides, even with a limited amount of effort) are given implementation preference. According to the UBA, the four work packages listed first below have priority, while Work Packages 1-4 were ranked with decreasing priority (i.e., Work Package 1 has the highest priority). The ranking was based on criteria such as the number of substances involved, application frequency, relevance for authorisation, public interest, political relevance and possible implications of the results for other regulatory areas.

Work Package 1 – Water pollution caused by entries from sewage treatment plants, including pollution caused by suspended matter/sediments

The substantial number of different applications that result in the entry of biocides into sewage treatment plants and the widespread use of these biocidal products by mainly private users have meant that UBA regards this particular entry path as critical when it comes to determining the levels of biocidal pollution in the environment. Entry also takes place continuously throughout the year.

The UBA believes that in the case of this module, the selected substances (see Table 6.1.5) should be analysed both in sewage treatment plants (influent, effluent) and in the associated waters. Depending on the substance properties, surface water samples and suspended matter and sediment samples in surface water must be taken and tested, in order fully understand the distribution of the substances in the sediment. The implementation of the proposed work package would thus provide an overview of the extent of the biocidal pollution, as well as the behaviour of the selected biocides along this entry path. The UBA believes that a representative number of at least 40 sewage treatment plants with their surface waters should be selected. This selection should be based on several criteria, including size class, development stage, sewer system, percentage of waste water in the waters, etc.); for more details, see Chapter 6.1.

The UBA will probably provide financial resources from the 2017 departmental research plan of the Federal Government (amount planned is 480,000 euros) to participate in the programme of the federal states for the study of pollutants from municipal sewage treatment plants, in order to ascertain the emissions, discharges and losses of priority substances for river basin units in Germany. With the help of these funds, the planned analysis of the sewage plant effluent samples from approximately 30 sewage treatment plants should be expanded to encompass approximately 20 biocides, making an essential contribution to the implementation of Work Package 1.

Additional studies of these proposed biocides in other surface waters, e.g. at measuring points where samples are taken during surface water monitoring procedures carried out by the federal states in accordance with the Water Framework Directive/Surface Water Ordinance, are recommended by the UBA as a supporting measure.

Work Package 2 – Water pollution through rainwater drainage (urban areas with a separate sewer system), including pollution caused by suspended matter/sediment

According to the UBA, this entry path should be considered as a priority for determining the biocidal pollution levels of waters, above all in urban areas. This is partly because the entries of the substances take place directly into the water without being preceded by an elimination process. On the other hand, there has been a steady increase in the use of biocidal material protection products in the building industry over many years now, and this would suggest that the relevance of this particular entry path for biocides into the environment has grown constantly.

The UBA is of the opinion that the selected substances (see Table 6.2.5) should be analysed in rainwater drainage systems and in the associated waters, within the framework of this module. According to the UBA, the implementation of this work package must not only include the testing of surface water samples, but also test samples of suspended matter and/or sediments in the surface water (depending on the substance properties involved), in order to better understand the distribution of substances in the sediment. If the proposed work package is implemented, an overview of the extent of the biocidal pollution and of the behaviour of the selected biocides along this entry path can be obtained. To this end, the UBA suggests that at least 20 rainwater drainage systems should be selected, based on a number of criteria (including the size of the connected building area, the types and ages of the buildings, the intermediate storage of the rainwater, the rainwater content in the waters, etc.). The measurements should encompass several rainfall events and the waters should also be sampled and tested in dry weather (see Chapter 6.2 for details).

As a supporting measure, the UBA recommends that other surface waters are analysed to determine the occurrence of the prioritised biocides, e.g. at measuring points, where surface water monitoring procedures are carried out by the federal states in accordance with the Water Framework Directive/Surface Water Ordinance.

Work Package 3 – Pollution of waters through other direct biocidal entries (especially active anti-fouling substances) including the pollution of suspended matter/sediments

The UBA considers the collection of data on the occurrence of active anti-fouling substances and transformation products to be very important within the framework of this work package. The alarming results of the nationwide active substance screening presented in Chapter 2 (see also UBA 2015a) are based solely on one single measuring procedure during which only the water phase was addressed while the sorption to suspended matter and sediments was not taken into consideration.

The UBA believes that marina operators and associations should be contacted to check whether or not new testing procedures may be carried out in the sportsboat harbours in which active biocidal substances have already been detected (approx. 30 marinas). Sampling and tests should be carried out immediately after the start of the season in spring and continue on into the main season. Since an accumulation of pollutants has often been observed in harbour sediments, the UBA recommends that samples of suspended matter or sediments be taken at the appropriate locations and tested for the prioritised biocides (see Table 6.3.5), depending on the substance properties (see Chapter 6.3 for details).

The UBA believes that the measurement of the prioritised biocides in other surface waters, e.g. at measuring points where samples are taken during surface water monitoring procedures carried out by the federal states in accordance with the Water Framework Directivce/Surface Water Ordinance, should be carried out as a logical supporting measure.

Work Package 4 – Pollution of groundwater beneath intensively-used agricultural areas on which liquid manure is spread including the pollution of drainage water from these areas

Since the quality of groundwater is of immense importance for the supply of drinking water, the UBA believes that the collection of data on this entry path is very important, also for precautionary reasons. In addition, the UBA is of the opinion that drainage water from intensively-used agricultural areas on which liquid manure is spread should be investigated. Since it is customary in some regions to drain off near-surface groundwater into the relevant waters by means of a drainage system, this direct entry into surface waters should not be neglected in these regions.

Within the framework of this module, at least 40 groundwater measuring points representative of intensively-used agricultural areas should be tested for the selected substances (see Table 6.4.5) (for details see Chapter 6.4). One possible criterion for the selection of the groundwater locations could be proven nitrate pollution at the sampling points. For the selection of the sampling sites, the study program 'Pharmaceuticals in the Environment' (BLAC 2003) could also be used for purposes of orientation. Regarding the possible pollution of drainage waters, the UBA is of the opinion that at least 10 samples should be examined for the priority substances on a regional basis. The point in time at which sampling takes place should be oriented on the existing agricultural management practice in the areas in question.

The UBA also considers the following **other modules** to be important for obtaining a comprehensive overview of environmental pollution caused by biocides, even if these are regarded as being of less priority than Work Packages 1-4. The sequence of these work packages should be regarded as a listing and should not specify a ranking by priority.

Pollution of riverbank filtrate

The UBA considers the testing of riverbank filtrates for the selected substances (see Table 6.5.5) to be very relevant since riverbank filtrate is of immense importance for the drinking water supply. Theoretically, all the biocides (a) that accumulate in the relevant surface waters via the various entry paths (sewage treatment plants, rainwater, other direct entries) and (b) the substance properties of which suggest that the level of retention in the ground passage is not sufficient to prevent their entry into the riverbank filtrate come into question here.

The UBA recommends testing riverbank filtrate samples from at least 15 waters. The selection should particularly be based on a higher proportion of wastewater in the body of water, or on the course of the body of water through predominantly urban areas (for details see Chapter 6.5).

Pollution of sewage sludges and soils treated with sewage sludges as well as absorption into terrestrial biota

The UBA considers the collection of data on the occurrence of selected biocides in sewage sludges, in soils treated with sewage sludge and in the corresponding terrestrial organisms to be important for completing the picture of biocidal environmental pollution. The findings of a previous UBA project (see Chapter 2) indicate that biocides sorbed to sewage sludge can accumulate in agricultural soils and terrestrial organisms.

In the opinion of the UBA, it would make sense to test at least 15 sewage sludge samples for the prioritised substances (see Table 6.6.5). Municipal sewage treatment plants, which are also tested in Work Package 1 (water pollution through entries from sewage treatment plants including pollution from suspended matter/sediments) should be tested for the biocides in question to the extent possible (for details see Chapter 6.6).

For the selection of soils treated with sewage sludge, it is necessary to first search for possible areas on which sewage sludge has been spread for many years on a regular basis. According to the UBA, it would be ideal to sample at least 10 of the relevant soils. The known permanent soil monitoring areas (BDFs) of the federal states should at least be used for testing purposes. In order to estimate the accumulation of substances in terrestrial organisms, the UBA recommends the collection and analysis of earthworms. Further suggestions for carrying out such examinations can be found in Chapter 6.6.

Pollution of soils treated with liquid manure and absorption into terrestrial biota, with a targeted study of individual liquid manures (where applicable)

Due to the large-scale and frequent use of liquid manure as a fertiliser for agricultural soils, the UBA considers it necessary to measure biocide residues in soils regularly treated with liquid manure and in the associated terrestrial biota, in order to obtain a comprehensive overview of the pollution levels of the terrestrial environment caused by biocides (for selected substances see Table 6.7.5).

For the selection of the corresponding soils, the UBA is of the opinion that the BDFs of the federal states should in any case be taken into consideration, since their history with liquid manure is known. In addition, the UBA recommends locating other areas that have been treated with liquid manure for many years, and which could be used for sampling, possibly immediately after the most recent treatment with liquid manure. According to the UBA, sampling of at least 30 soils would be ideal. The UBA recommends the collection and analysis of earthworms to assess the accumulation of the substances in terrestrial organisms (for details see Chapter 6.7).

Since liquid manure in Germany is a commodity that is transported and mixed over long distances, it should not be assumed that the path from biocidal application → liquid manure→ field can be clearly traced. The UBA is therefore of the opinion that to obtain a full picture of the possible contamination of liquid manure through biocides, it is necessary to test a series of liquid manure samples from farms which have been known to use biocides regularly (e.g. stall disinfectants, insecticides). The selection should address (inter alia) different animal species and agricultural management practices. Detailed proposals for conducting tests are also listed in Chapter 6.7.

Pollution of aquatic biota (limnic ecosystem)

The accumulation of biocides in aquatic organisms depends on the substances' properties as some examples have already confirmed, e.g. alarming rodenticide levels found in fish (see Chapter 1). This aspect should therefore not be neglected for precautionary reasons alone when the pollution of the aquatic environment (limnic ecosystem) through biocides is assessed. For passive monitoring with fish, the UBA considers that it would be useful to test 10 fish for the priority substances from at least 40 different sampling points (see Table 6.8.5). Mussels, as a representative of the group of primary consumers can be tested using passive as well as active monitoring at the selected sampling points. In this case, biota samples should be selected from water bodies which have a higher proportion of waste water or which mainly flow through urban areas (for details see Chapter 6.8). According to the UBA, existing biota samples stored in the archive of the ESB can also provide a suitable basis for trend investigations.

Pollution of soils in urban areas due to direct entries (e.g. rodenticides, ant prevention products, wood preservation products, rainwater infiltration)

To date, no data on the biocidal pollution of soils exists for these locally-restricted entries. However, the UBA is aware that material protection products containing biocides are already state-of-the-art in the construction industry and that local rainwater infiltration is explicitly promoted in many cities. On the other hand, many insecticides, such as ant prevention products are widely used by professional and private users around buildings. Both of these considerations have led the UBA to believe that the collection of data on the local occurrence of these biocides in soils of urban areas should also be taken into account.

In this module, the UBA believes it would make sense to use a series of small projects tailored directly to the corresponding biocide application or to the entry path. One partial aspect, which is of regional importance, would be the analysis of soils into which rainwater (that originates from façades and roofs) infiltrates; this analysis could include the groundwater near the surface. In this context, both the methods of surface infiltration and the trough percolation of rainwater are of interest, since both methods affect part of the garden soil. When selecting the soils, it is of course important to ensure that the buildings in question also contain biocides on their façades or roofs. Since the biocides used are known, the analysis of the soil samples can be restricted to these active substances and possibly to relevant transformation products.

The UBA believes that a second project, which would also be of interest for environmental risk assessment would be the testing of soils for residues of local biocide applications, e.g. after rodenticides or insecticides have been applied, or around wooden structures. However, according to the UBA, it would be necessary to optimise the sampling design before the project was carried out, since no standard sampling could be performed. Since the biocides used here are also known, the analysis of the soil samples can again be restricted to these active substances and possibly to their relevant transformation products.

4 Selection of the substances (prioritisation)

As a further aid for the future implementation of the work packages described in Chapter 3, up to 25 relevant active substances and transformation products were selected for each work package. The UBA is of the opinion that the occurrence of these 25 active substances in the environment should be prioritised for testing.

During the prioritisation process, the UBA used the procedure explained in detail below to address all the active biocidal substances, which were authorised pursuant to the EU Biocidal Products Regulation, or for which an initial biocidal assessment report was submitted by the end of May 2016 (pursuant to EU Biocidal Products Regulation). In addition to the active substances themselves, all the relevant transformation products of these active substances were considered, provided that they had been clearly identified and addressed in the risk assessment. A total of 320 substances were included in the prioritisation process. However, it must be noted that a certain number of biocidal active substances (particularly from the disinfectants and materials protection segments) have not been considered in the database, since the required data (EU assessment reports) is not yet available.

Since the UBA believes that organic-chemical biocides are particularly for the prioritisation process, 77 active substances were initially removed from the existing data pool and were not further considered. These active substances included:

- micro-organisms
- fumigants
- fast-reacting substances (e.g. formaldehyde, ozone)
- simple and naturally-occurring acids (e.g. lactic acid)
- inorganic substances (e.g. silver, iodine)

In contrast, metallo-organic compounds and metal complexes with organic content were considered relevant for the selection.

For the purpose of prioritisation, the UBA adopted the concept for the identification of relevant active biocidal substances. This concept was developed during the research project 'Environmental Measuring Programme for Biocides' and has been slightly adapted to address current developments in the assessment of biocides. In order to estimate the relevance of a substance, three areas are basically tested in the prioritisation scheme which is used:

1) Estimated emitted quantity
2) Eco-toxicological effects
3) Entry into and behaviour in the affected environmental compartment.

Several criteria were specified for the testing of the individual areas. Depending on the application areas and the properties of the substances, these are given more or less points for each criterion. The points are added within an area and the results of the three areas are then multiplied.

The following criteria are included in the testing of the areas:

1. Estimated emitted quantity[11]

    - Number of emission-relevant product types in which the substance is used
    - Number of products containing the active substance that are registered with the BAuA (German Federal Institute for Occupational Safety and Health)[12]

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[11] Since the EU-wide tonnage of biocidal active substances is unknown, the estimated emitted quantity was calculated using alternative criteria, which, however, do not necessarily reflect the exact distribution and application data.

[12] All biocidal products marketed in Germany must be registered in accordance with the Biocide Reporting Ordinance (Link: http://www.baua.de/de/Chemikaliengesetz-Biozidverfahren/Biozide/Produkt/Meldeverordnung.html).

- ► EU production or import quantity of substances registered in the context of REACH, if published[13]

2. Eco-toxicological effects

- ► PNEC[14] for aquatic organisms
- ► Fulfilment of the T criterion (toxicity)
- ► Bio-accumulation behaviour
- ► Suspected endocrine-disruptive properties[15]

3. Entry into and behaviour in the affected environmental compartment

- ► Number of product types in which the substance is used and which are relevant for a work package
- ► Bio-degradability
- ► Fulfilment of the P criterion (persistence)

The points given for the individual criteria are contained in Appendix 1.

The UBA has subsequently specified other criteria to ensure that a list of relevant substances tailored to the work packages presented in Chapter 3 can be proposed. These other filter criteria are presented here as examples for Work Package 1, 'Water pollution caused by entries from sewage treatment plants, including pollution caused by suspended matter/sediments':

- ► Use in product types where an emission into the sewage treatment plant can be expected
- ► Not readily bio-degradable
- ► Half-time hydrolysis ≥ 48 hours (at 12°C)
- ► Half-time in the water sediment system ≥ 48 hours (12°C)
- ► Distribution coefficient of water-organic substances in soil (Koc) < 5000
- ► Also for the sediment: Koc ≥ 1000

The additional filter criteria used for tailoring the selection of the substances to the other work packages are also contained in Appendix 1.

A list of relevant substances and transformation products has thus been created for each of the work packages described in Chapter 3. The UBA had experts assess the validity of the list and substances were subsequently deleted from the list or added to it, if specific indications of any relevance were found, independent of the described prioritisation procedure. These additions were marked in the lists in question.

All the individual lists are contained in the respective work package in Chapter 6. The UBA views these substance lists as recommendations and generally assumes that the selection of the actual analytes can be once again specifically discussed during the concrete implementation of the recommendations.

In the overall view of the lists, it can be seen that they contain many active biocidal substances or transformation products, which have either not been addressed or hardly considered during sampling and testing. One example of this is the group of isothiazolinones, the representatives of which (benzisothiazolinone (BIT) and octhilinone (OIT)) have been identified as being relevant for the sewage treatment plant entry path or the rainwater path. The substance group of isothiazolinones is known for its undesirable effects, such as a high level of toxicity for aquatic organisms. Isothiazolinones are

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[13] Link to the ECHA database: http://echa.europa.eu/de/information-on-chemicals/registered-substances.

[14] Predicted no effect concentration (predicted concentration of a substance up to which no environmental effects become evident).

[15] Evaluation is carried out according to transition criteria for substances with endocrine-disruptive properties, see Biocidal Products Regulation, Art. 5.

used to a considerable extent as preservatives against micro-organisms in cleansing substances, lacquers, paints and wood preservatives. Other uses are in paper production, cooling and process water and anti-microbially-finished textiles. Some substances can also cause sensitisation of the skin (contact allergens) in humans through direct contact or via the air.

The lists of substances also contain a number of well-known substances, which are also used as active substances in plant protection products; some of these are already regulated in the Surface Water Ordinance or Water Framework Directive. Examples here are diuron or isoproturon, which the UBA has identified as priorities for sewage treatment plant and rainwater entry paths. However, the UBA still considers it very important to collect additional data on these substances, and in particular for their specific entry paths, in order to assess the relevance of the entries resulting from biocide applications compared to those resulting from the use of plant protection products. In addition, many substances have only been measured in the water phase, but the testing of the pollution levels in sediment has been neglected.

Since the above-mentioned prioritisation criteria have been applied, the UBA now view the substance permethrin as being relevant for monitoring due to its environmental impact on virtually all environmental media. This is the same conclusion as the one reached by e.g. the Joint Research Centre (JRC). The report of the JRC also describes permethrin as an SVHC, due to its biocidal properties. This EU Commission report created the first monitoring list during the revision of the lists of priority substances pursuant to the Water Framework Directive (JRC 2015). However, the substance was not included in the monitoring list, since sufficient monitoring data was already available for surface waters at that point in time. Permethrin was nevertheless identified as a highly-ranked candidate for the revised list of prioritised substances (JRC 2016) on the basis of the evidence provided by the data.

5 Quality assurance and evaluation

During the preparation of this recommendation, the UBA also tackled the fundamental issues of quality assurance and evaluation. However, it is recommended that discussions are again held on these issues, with a view to tailoring them for the possible future implementation of the recommendations.

The UBA has minimised the scope and frequency of sampling proposed in Chapter 6 for each work package, while retaining an effective representation of the results. As a basis for its considerations, the UBA drew upon the results of the special measuring programme 'Pharmaceuticals in the Environment'[16]. In the case of some work packages, site selection involves increased research, e.g. in the case of soils treated with sewage sludge and liquid manure. The UBA has taken this aspect into account in the proposals.

In order to reduce the likelihood of substances being classified as a priority due to the specification of filter criteria in the prioritisation concept, even although they will not be detectable under realistic conditions in the environment, the UBA employed experts to validate for plausibility all the substance lists that resulted from the prioritisation concept.

The recommendations for measuring locations or dates were chosen in such a way that the unwitting selection of inappropriate measuring points or dates for some selected substances is avoided. This is to prevent the creation of the false impression that they could not be detected in the environment, although they possibly would have been detected if other dates and measuring points had been selected. In the recommendations in Chapter 6, for example, the main focus of the sampling and testing is oriented on urban areas or on intensively-farmed agricultural soils. The possibility that only 'hot spots' are used as measuring points – meaning locations that do not provide a realistic picture of the situation in Germany – should also be prevented as much as possible. For this reason, the UBA recommends e.g. the testing of sewage treatment plants that belong to at least two distinct size classes.

Regarding the evaluation of the findings from the individual modules, the UBA recommends the formation of a working group (WG); this was the case, for example, during the special measuring programme 'Pharmaceuticals in the Environment'. The task of this WG should include the interpretation of the data and the preparation of a final report. To enable a more efficient evaluation procedure, the UBA is willing to organise the acquired data in a database.

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16 Link to the final report: http://www.blac.de/servlet/is/2146/P-2b.pdf

6 Detailed proposals for carrying out measurements

6.1 Work Package 1 – Water pollution caused by entries from sewage treatment plants, including pollution caused by suspended matter/sediments

6.1.1 Sample volume

How many measuring points are necessary?

- at least 40 sewage treatment plant sites (sampling in the sewage treatment plants and waters)

How often and at what intervals should measurements be carried out?

- at least 4 times a year (spring, summer, autumn, winter) (sampling in the sewage treatment plants and waters)
- the interval between the seasonal samples taken should ideally be 3 months
- where appropriate, also consider different weather events (long dry periods, severe rainfall); this is particularly useful in the case of a combined sewer system

6.1.2 Sampling points

How are the test sites selected?

- The sewage treatment plant sites should be selected on the basis of the following points:
  - Municipal sewage treatment plant
  - Size class (at least 3 varied sizes; <10,000 population, >10,000 to 100,000 pop., >100,000 pop.)
  - Development stage (at least stages 3 and 4)
  - Sewer system (separate, combined)
  - The highest possible proportion of wastewater water in the water body
  - Regarding waters: preferably select urban areas, with the lowest possible proportion of industrial wastewater

At which locations should the samples be taken?

- Per location:
  - Sewage plant influent
  - Sewage plant effluent
  - Waters before the introduction of treated wastewater
  - Waters after the introduction of treated wastewater (with complete mixing)
  - Suspended matter (or sediment) prior to introduction
  - Suspended matter (or sediment) after introduction (with complete mixing)

How should the samples be taken?

- In the sewage treatment plant, create an effluent-proportional, weekly mixed sample (Mo-Sun) from 24-hour mixed samples (e.g. composed of samples taken at between 5 and 30 intervals using an automatic sampler)
- ideally, also take an effluent-proportional weekly mixed sample from the surface water
- Filter the water phases through suitable filters
- When calculating load levels, the effluent data should be collected at the same time where possible (sewage treatment plant, waters)
- Take samples of suspended matter using a sediment trap (or take samples of near-surface sediment)

- The fraction < 63 µm is to be used for sediment analyses pursuant to the Surface Water Ordinance

Sample methods based on:

- DIN 38402-11: 2009 Sampling of wastewater
- DIN ISO 5667-14: 2013 Instructions for quality assurance when taking and handling water samples
- DIN EN ISO 5667-1: 2007 Part 1, Instructions for the preparation of sampling programs and sampling techniques
- DIN 38402-15: 2010 Part 15, Sampling from flowing waters
- DIN EN ISO 5667-3: 2013 Part 3, Conservation and handling of water samples
- A procedural guideline for sampling with suspended matter traps has been developed within the framework of the ESB.
 (www.umweltprobenbank.de/upb_static/fck/download/SOP_Schwebstoffe.pdf)
- WFD Guidance on the chemical monitoring of sediment and biota, EC 2010)
- LAWA (2016) LAWA-AO Framework Concept Monitoring Part B, Assessment Principles and Methodology Work Paper IV.4 Recommendation for Suspended Matter and Sediment Studies at Survey Sites pursuant to the Cabinet Draft of the Ordinance on the Protection of Surface Waters of December 16, 2015.

6.1.3 Analytical requirements

Suitable analytical methods

- Requirements for processes and laboratories are described, e.g. in the Surface Water Ordinance
- GC-MS or HPLC-MS methods in accordance with the substance properties
- Analysis methods from the EU assessment report on the respective substance can be used where applicable
- Other examples of analytical methods in the DBU report: 'Development of a balancing instrument for the entry of pollutants from municipal sewage treatment plants into water bodies' (DBU 2014[17])

Availability of isotope-labelled reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)
- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- It should be noted that biocides which are also used as PSM are available as labelled reference substances
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.1.4 Measuring programmes that are possibly relevant

- Surface water monitoring of the federal states pursuant to the Water Framework Directive/Surface Water Ordinance

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[17] Final report: https://www.dbu.de/OPAC/ab/DBU-Abschlussbericht-AZ-29630-01.pdf

- Usage of the samples collected during the self-monitoring procedures of sewage treatment plant operators
- Extended monitoring project for the second survey of emissions, discharges and losses of priority substances for the river basin units in Germany (financed by the federal states, from 2016) (Federal State Ad Hoc WG 2016) [18]
- BLAC special measuring programme 'Pharmaceuticals in the Environment' (2003)[19]
- ESB (suspended matter samples)

6.1.5 Prioritised substances

Table 1: Prioritised substances for Work Package 1. The substances in the shaded grey lines have been prioritised for both the water phase and for sediments; substances in the shaded green lines are mainly relevant for the water phase. TP = Transformation Product

Substance	CAS no.	Product Type[20] pursuant to the Biocidal Products Regulation	Quality parameter [21] in µg/L or µg/kg ww Type	Value
Alkyldimethylbenzyl ammonium chloride (ADBAC/BKC)[a)]	68424-85-1 68391-01-5 85409-22-9	1, 2, 3, 4, 8, 10, 11, 12, 22	$PNEC_{Water}$ $PNEC_{Sediment}$	0.415 3570
2-Aminobenzimidazole (2-AB, TP of carbendazim)	934-32-7	7, 9, 10	$PNEC_{Water}$	0.15*§
1.2-Benzisothiazolin-3(*2H*)-on (BIT)	2634-33-5	2, 6, 9, 11, 12, 13	$PNEC_{Water}$	1.1§
Brodifacoum[b)]	56073-10-0	14	$PNEC_{Water}$ $PNEC_{Sediment}$	0.04 unknown
Carbendazim[c)]	10605-21-7	7, 9, 10	JD-UQN ZHK-UQN $PNEC_{Water}$	0.2 0.7 0.15§
Diethyltoluamide (DEET)	134-62-3	19	$PNEC_{Water}$	4.3
Diclosan (DCPP)	3380-30-1	1, 2, 4	$PNEC_{Water}$ $PNEC_{Sediment}$	0.93 192
Didecyldimethyl ammonium chloride (DDAC)[a)]	68424-95-3 7173-51-5	1, 2, 3, 4, 6, 8, 10, 11, 12	$PNEC_{Water}$ $PNEC_{Sediment}$	1 3560

18 Link to the final report on the first survey: http://www.umweltbundesamt.de/publikationen/bestandsaufnahme-der-emissionen-einleitungen

19 Final report: http://www.blac.de/servlet/is/2146/P-2b.pdf

20 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

21 Quality parameters are: Environmental quality standards (UQN), which are listed as annual average values (JD-UQN) in Appendices 6 and 8 of the OGewV (2016) or as maximum permissible concentration (ZHK-UQN), or the PNEC for water ($PNEC_{water}$) and for suspended matter/sediment ($PNEC_{sediment}$) from the Biocidal Products Regulation implementation procedure.

Difethialon[b)]	104653-34-1	14	$PNEC_{Water}$ $PNEC_{Sediment}$	0.0044 44
Diuron[e)g)]	330-54-1	7, 10	JD-UQN ZHK-UQN	0.2 1.8
Imazalil[g)]	35554-44-0	3	$PNEC_{Water}$	1.1[§]
Imidacloprid[c)]	138261-41-3	18	JD-UQN ZHK-UQN $PNEC_{Water}$	0.002 0.1 0.0048
Isoproturon[e)g)]	34123-59-6	7, 10	JD-UQN ZHK-UQN	0.3 1
Methyl-diclosan (TP of diclosan)		1, 2, 4	$PNEC_{Water}$ $PNEC_{Sediment}$	0.93* 202
Methyltriclosan (TP of triclosan)[h)]	4640-01-1	1[§]	$PNEC_{Wasser}$	0.05*
Octhilinon (octylisothia-zolinone, OIT)	26530-20-1	6, 7, 8, 9, 10, 11, 13	$PNEC_{Water}$ $PNEC_{Sediment}$	0.0136[§] 0.03[§]
Permethrin[f)]	52645-53-1	8, 9, 18	$PNEC_{Water}$ $PNEC_{Sediment}$	0.000094 0.00289
Permethrinic acid (DCVA, cis/trans, TP of various pyrethroids, e.g. permethrin, cyperme-thrin, cyfluthrin)	55701-05-8	8, 18	$PNEC_{Water}$	15
Prallethrin	103065-19-6	18	$PNEC_{Water}$ $PNEC_{Sediment}$	0.0062 unknown
Propiconazol[c)]	60207-90-1	7, 8, 9	JD-UQN $PNEC_{Water}$ $PNEC_{Sediment}$	1 6.8 54
2-pyridine-sulfonic acid (PSA, TP of Na-/Cu-/Zn-pyrithione)[i)]	15103-48-7	2, 6, 7, 9, 10, 13, 21	$PNEC_{Sea\ water}$	5.46
Tebuconazole	107534-96-3	7, 8, 10	$PNEC_{Water}$ $PNEC_{Sediment}$	1 550
Terbutryn[e)g)]	886-50-0	7, 9, 10	JD-UQN ZHK-UQN	0.065 0.34
Thiabendazole	148-79-8	7, 8, 9, 10	$PNEC_{Water}$ $PNEC_{Sediment}$	1.2 30
1,2,4-Triazole (TP of propiconazole (among others))	288-88-0	7, 8, 9	$PNEC_{Water}$	6.8*
Triclosan[c)h)]	3380-34-5	1[§]	JD-UQN ZHK-UQN $PNEC_{Water}$	0.02 0.2 0.05

[a)] Not included in the prioritisation list due to its strong sorption on sewage sludge and its readily degradable properties in water, but there are many products on the market, so continuous entries of this substance into the environment are to be expected.
[b)] PBT substance with strong sorption on sewage sludge, therefore not included in the prioritisation list, but a preliminary study detected the substance in fish, so entries into surface waters must have taken place.
[c)] Included in Appendix 6 of the OGewV, 2016.
[d)] DEET is readily degradable, therefore not included in the prioritisation list, but it has already been detected in relevant concentrations in sewage treatment plants.
[e)] Included in Appendix 8 of the OGewV, 2016, priority substance according to the WFD.
[f)] PBT substance with a prominent level of sorption, therefore it is not included in the prioritisation list, but its usage would suggest entry via sewage treatment plants; this substance was also found in surface waters.
[G)] No complete EU assessment reports exist for these substances to date; however, based on their uses and the results of individual measurements, it is likely that they enter the environment.
[h)] Triclosan has now been given an 'unauthorised' status for all product types. Nevertheless, a number of products may still be sold within the sell-off period. In the past, Triclosan was widely used in treated products, therefore entries may still occur via these applications.
[i)] Considered to be readily degradable, but there are very many products on the market, so continuous entries into the environment are to be expected. The metabolite PSA was also selected for the sediment, since accumulations have been observed in micro- and mesocosm studies.
[*]No specific PNEC values have been derived for these substances, because the transformation products were assessed as being equally or less toxic when compared to the original substances. This is why the PNEC of the original substance has been provisionally listed in this table.
[§] The values listed are only provisional, since the assessment report has not yet been finalised.

6.2 Work Package 2: – Water pollution caused by rainwater drainage (urban areas with separate sewer systems), including the pollution caused by suspended matter/sediments

6.2.1 Sample volume

How many measuring points are necessary?

- At least 10 rainwater sewers that drain directly into water bodies (sampling in the rainwater sewers and water bodies)
- In addition, at least 10 rainwater sewers, the waters of which are temporarily stored in rainwater collecting basins (sampling performed in collecting basins and water bodies)

How often and at what intervals should measurements be carried out?

- At least 6 rainfall events (involving rainwater runoff) of varying intensities if possible (sampling in rainwater sewers/rainwater collecting basins and water bodies)
- Sampling should preferably take place in spring or autumn
- In addition, sampling of the water should take place at least once during a longer period of dry weather

6.2.2 Sampling points

How are the sampling points selected?

- Rainwater sewers should be selected on the basis of the following criteria:
  - Size of the adjoining building area
  - Types of buildings (e.g. old buildings)
  - Ages of buildings
  - Intermediate storage of the rainwater
  - Rainwater content in the body of water

At which locations should the samples be taken?

- Per location:
  - Rainwater runoff at the discharge point (direct discharges or discharges into the rainwater collecting basin)
  - Waters before the confluence of the rainwater sewer
  - Waters after the confluence of the rainwater sewer, with complete mixing
  - Suspended matter (or sediment) before confluence
  - Suspended matter (or sediment) after confluence, with complete mixing

How should the samples be taken?

- Event-based sampling at the direct discharger using an automatic sampler
- Sampling from rainwater collecting basin no later than 1 day after the rainfall event
- Sampling of the rainwater-affected water body during or directly after the precipitation event
- When calculating load levels, the discharge data should be collected at the same time if possible (direct discharger, waters)
- Filter the water phase through suitable filters
- Take samples of transported suspended matter using sediment traps (or take samples of near-surface sediment)
- The fraction < 63 µm is to be used for sediment analyses pursuant to the Surface Water Ordinance

Sample methods based on:

- WFD – Guidance on surface water chemical monitoring, EC 2009)
- DIN EN ISO 5667-1: 2007 Part 1, Instructions for the preparation of sampling programs and sampling techniques
- DIN 38402-15: 2010 Part 15, Taking samples from flowing waters
- DIN EN ISO 5667-3: 2013 Part 3, Conservation and handling of water samples
- A procedural guideline for sampling with suspended matter traps has been developed within the framework of the ESB. (www.umweltprobenbank.de/upb_static/fck/download/SOP_Schwebstoffe.pdf)
- WFD – Guidance on the chemical monitoring of sediment and biota, EC 2010)
- LAWA (2016) LAWA-AO Framework Concept Monitoring Part B, Assessment Principles and Methodology Work Paper IV.4 Recommendation for Suspended Matter and Sediment Studies at Survey Sites pursuant to the Cabinet Draft of the Ordinance on the Protection of Surface Waters of December 16, 2015.

6.2.3 Analytical requirements

Suitable analytical methods

- GC-MS or HPLC-MS methods in accordance with the substance properties
- Requirements for processes and laboratories are described in the Surface Water Ordinance
- Analysis methods from the EU assessment report on the respective substance can be used where applicable
- Analysis methods from the project: 'Relevance of organic trace substances in the Berlin rainwater runoff system' from the Competence Centre Wasser Berlin (Wicke et al., 2015)

Availability of isotope-labelled, reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)
- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- It should be noted that biocides which are also used as PSM are available as labelled reference substances
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.2.4 Measuring programmes that are possibly relevant

- Surface water monitoring of the federal states pursuant to the Water Framework Directive/Surface Water Ordinance
- ESB (suspended matter samples)
- Project: 'Relevance of organic trace substances in the Berlin rainwater runoff system' from the Competence Centre Wasser Berlin (Wicke et al., 2015) [22]

[22] Link to the final report: http://www.kompetenz-wasser.de/index.php?id=568&type=0&jumpurl=fileadmin%2Fuser_upload%2Fpdf%2Fforschung%2FOgRe%2FAbschlussbericht_OgRe_final_rev2.pdf

6.2.5 Prioritised substances

Table 2: Prioritised substances for Work Package 2. The substances in the shaded grey lines have been prioritised for both the water phase and for sediments; substances in the shaded green lines are mainly relevant for the water phase. TP = transformation product

Substance	CAS no.	Product Type[23] pursuant to the Biocidal Products Regulation	Quality parameter [24] in µg/L or µg/kg ww Type	Value
Alkyldimethylbenzyl ammonium chloride (ADBAC/BKC)[c)]	68424-85-1 68391-01-5 85409-22-9	1, 2, 3, 4, 8, 10, 11, 12, 22	$PNEC_{Water}$ $PNEC_{Sediment}$	0.415 3570
2-Aminobenzimidazole (2-AB, TP of Carbendazim)	934-32-7	7, 9, 10	$PNEC_{Water}$	0.15*§
1.2-Benzisothiazolin-3(2H)-on (BIT)	2634-33-5	2, 6, 9, 11, 12, 13	$PNEC_{Water}$	1.1
Brodifacoum	56073-10-0	14	$PNEC_{Water}$ $PNEC_{Sediment}$	0.04 unknown
Bromadiolon	28772-56-7	14	$PNEC_{Water}$ $PNEC_{Sediment}$	0.017 830
Carbendazim[a)]	10605-21-7	7, 9, 10	JD-UQN ZHK-UQN $PNEC_{Water}$	0.2 0.7 0.15§
2-chloro-2- (n-octylcarbamoyl) -1-ethenesulfonic acid (TP of DCOIT)		7, 8, 9, 10, 11, 21	$PNEC_{Water}$ $PNEC_{Sediment}$	0.034* 410*
Cypermetrin	52315-07-8	8, 18	JD-UQN ZHK-UQN $PNEC_{Water}$ $PNEC_{Sediment}$	0.00008 0.0006 0.04 50
Didecyldimethylammoniumchloride (DDAC)[c)]	68424-95-3/7173-51-5	1, 2, 3, 4, 6, 8, 10, 11, 12	$PNEC_{Water}$ $PNEC_{Sediment}$	1 3560
Difenacoum	56073-07-5	14	$PNEC_{Water}$ $PNEC_{Sediment}$	0.06 2510
Difethialon	104653-34-1	14	$PNEC_{Water}$ $PNEC_{Sediment}$	0.0044 44
Diuron[b)d)]	330-54-1	7, 10	JD-UQN ZHK-UQN	0.2 1.8

23 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

24 Quality parameters are: Environmental quality standards (UQN), which are listed as annual average values (JD-UQN) in Appendices 6 and 8 of the OGewV (2016) or as maximum permissible concentration (ZHK-UQN), or the PNEC for water ($PNEC_{Water}$) and for suspended matter/sediment ($PNEC_{Sediment}$)

Flocoumafen	90035-08-8	14	$PNEC_{Water}$ $PNEC_{Sediment}$	0.07 0.02
Isoproturon[b)d)]	34123-59-6	7, 10	JD-UQN ZHK-UQN	0.3 1
Octhilinon (Octylisothia-zolinone, OIT)	26530-20-1	6, 7, 8, 9, 10, 11, 13	$PNEC_{Water}$ $PNEC_{Sediment}$	0.0136[§] 0.03[§]
Permethrin	52645-53-1	8, 9, 18	$PNEC_{Water}$ $PNEC_{Sediment}$	0.000094 0.00289
Permethrinic acid (DCVA, cis/trans, TP of various py-rethroids, e.g. permethrin, cypermethrin, cyfluthrin)	55701-05-8 59042-49-8 59042-50-1	8, 18	$PNEC_{Water}$	15
d-Phenotrin	26046-85-5	18	$PNEC_{Water}$ $PNEC_{Sediment}$	0.047 129
Propiconazol [a)]	60207-90-1	7, 8, 9	JD-UQN $PNEC_{Water}$ $PNEC_{Sediment}$	1 6.8 54
Tebuconazole	107534-96-3	7, 8, 10	$PNEC_{Water}$ $PNEC_{Sediment}$	1 550
Terbutryn[b)d)]	886-50-0	7, 9, 10	JD-UQN ZHK-UQN	0.065 0.34
1,2,4-Triazole (TP of pro-piconazole (among oth-ers))	288-88-0	7, 8, 9	$PNEC_{Water}$	6.8*

[a)] Included in Appendix 6 of the OGewV, 2016
[b)] Included in Appendix 8 of the OGewV, 2016, priority substance pursuant to the WFD
[c)] Not included in the prioritisation list due to strong sorption on sewage sludge and its readily degradable properties in water, but there are many products on the market, so continuous entries into the environment are to be expected.
[d)] To date, no complete EU assessment reports exist for these substances; but based on their uses and the results of individual measurements, it is highly probable that they enter the environment.
[*]No specific PNEC values have been derived for these substances, because the transformation products were assessed as being equally or less toxic when compared to the original substances. This is why the PNEC of the original substance has been provisionally listed in this table.
[§] The values listed are only provisional, since the assessment report has not yet been finalised.

6.3 Work Package 3 – Pollution of waters through other direct biocidal entries (especially anti-fouling substances) including the pollution of suspended matter/sediments

6.3.1 Sample volume

How many measuring points are necessary?

- At least 30 marinas (based on the results of the UBA research project 'Ensuring the reliability of the anti-fouling exposure assessment within the framework of the EU biocide authorisation procedure based on the current situation in German inland waters for the utilisation phase in the area of sportsboat harbours' [25])

How often and at what intervals should measurements be carried out?

- Waters: At least 4 times a year – immediately after the start of the season in the spring, during the main season in the summer, at the end of the season in autumn and in the winter; the ideal scenario would be 12 measuring points per year
- Sediment (or suspended matter): Twice a year: in spring and in autumn

6.3.2 Sampling points

How are the sampling sites selected?

- Distinction between marinas on coastal and inland waters, considering the following aspects:
  - Public and closed marinas
  - Marinas with small to large water volumes
  - Marinas with a few to many moorings
  - Marinas with strong or weak currents
- UBA recommendation: If possible, re-sampling of the marinas where biocides were found during the above-mentioned UBA research project.

At which locations should the samples be taken?

- Per location:
  - Surface water sample in the marina
  - Sediment (or suspended matter) in the marina

How should the samples be taken?

- Filter the water phase through suitable filters
- Sample the near-surface sediments (or remove suspended matter using sediment traps)
- The fraction < 63 µm is to be used for sediment analyses pursuant to the Surface Water Ordinance

[25] Link to the final report: https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_68_2015_sicherung_der_verlaesslichkeit_der_antifouling_0.pdf

Sample methods based on:

- WFD – Guidance on surface water chemical monitoring, EC 2009)
- DIN EN ISO 5667-1: 2007 Part 1, Instructions for the preparation of sampling programs and sampling techniques
- DIN 38402-15: 2010 Part 15, Sampling from flowing waters
- DIN EN ISO 5667-3: 2013 Part 3, Conservation and handling of water samples
- A procedural guideline for sampling with suspended matter traps has been developed within the framework of the ESB www.umweltprobenbank.de/upb_static/fck/download/SOP_Schwebstoffe.pdf)
- WFD – Guidance on the chemical monitoring of sediment and biota, EC 2010
- LAWA (2016) LAWA-AO Framework Concept Monitoring Part B, Assessment Principles and Methodology Work Paper IV.4 Recommendation for Suspended Matter and Sediment Studies at Survey Sites pursuant to the Cabinet Draft of the Ordinance on the Protection of Surface Waters of December 16, 2015.

6.3.3 Analytical requirements

Suitable analytical methods

- Requirements for processes and laboratories are described in the Surface Water Ordinance
- GC-MS or HPLC-MS methods in accordance with the substance properties: e.g. Wick et al. (2010): HPLC-MS multi-method for active biocidal substances (e.g. for cybutryn and DCOIT)
- Giráldez et al. (2013): Method based on ‘stir bar sorptive extraction’; e.g. for dichlofluanide, DCOIT and cybutryn)
- Analysis methods from the EU assessment report on the respective substance can be used where applicable
- Analysis methods from the UBA research project ‘Ensuring the reliability of the anti-fouling exposure assessment within the framework of the EU biocide authorisation procedure based on the current situation in German inland waters for the utilisation phase in the area of sportsboat harbours’
- Analysis methods from the project, ‘First Austrian Case Study on Anti-Fouling Agents in the Environment' (Environment Agency Austria, Hautzenberger et al., 2015) [26]

Availability of isotope-labelled, reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)
- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.3.4 Measuring programmes that are possibly relevant

- Surface water monitoring of the federal states pursuant to the Water Framework Directive/Surface Water Ordinance

[26] Link to the final report: http://www.umweltbundesamt.at/aktuell/presse/lastnews/news2015/news_150713/

- The UBA research project, 'Ensuring the reliability of the anti-fouling exposure assessment within the framework of the EU biocide authorisation procedure based on the current situation in German inland waters for the utilisation phase in the area of sportsboat harbours'
- The project 'First Austrian Case Study on Anti-Fouling Agents in the Environment' (Environment Agency Austria, Hautzenberger et al., 2015)
- ESB (suspended matter samples)

6.3.5 Prioritised substances

Table 3: Prioritised substances for Work Package 3. The substances in the shaded grey lines have been prioritised for both the water phase and for sediments; substances in the shaded green lines are mainly relevant for the water phase. TP = transformation product

Substance	CAS no.	Product Type[27] pursuant to the Biocidal Products Regulation	Quality parameter [28] in µg/L or µg/kg ww Type	Value
2-chloro-2- (n-octylcarbamoyl) -1-ethenesulfonic acid (TP of DCOIT)		7, 8, 9, 10, 11, 21	$PNEC_{Water}$ $PNEC_{Sediment}$	0.034* 410*
CL322,250 (TP of talopram)		21	$PNEC_{Water}$ $PNEC_{Sediment}$	6.9 1720
Cybutryne (irgarol)[a)]	28159-98-0	21	JD-UQN ZHK-UQN $PNEC_{Water}$ $PNEC_{Sediment}$	0.0025 0.016 0.002 9.57×10^{-4}
N'N-dimethylsulfamide (DMS, TP von tolylfluanid)	3984-14-3	7, 8, 21	$PNEC_{Water}$ $PNEC_{Sediment}$	10000 80
N,N-dimethyl-N'-phenylsulfamide (DMSA, TP of dichlofluanide)	4710-17-2	7, 8, 21	$PNEC_{Water}$	194
Dimethyltolylsulfamide (DMST, TP of tolylfluanid)	66840-71-9	7, 8, 21	$PNEC_{Water}$	140
Ethylene thiourea (ETU, TP of zineb)	96-45-7	21	$PNEC_{Water}$	21.6
GS 26575 (TP of cybutryne)[a)]		21	$PNEC_{Water}$ $PNEC_{Sediment}$	0.002* 9.57×10^{-4}*
Medetomidine	86347-14-0	21	$PNEC_{Water}$ $PNEC_{Sediment}$	0.002 0.10

27 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

28 Quality parameters are: Environmental quality standards (UQN), which are listed as annual average values (JD-UQN) in Appendices 6 and 8 of the OGewV (2016) or as maximum permissible concentration (ZHK-UQN), or the PNEC for water (PNECwater) and for suspended matter/sediment (PNEC sediment) from the Biocidal Products Regulation implementation procedure.

2-pyridine-sulfonic acid (PSA, TP of Cu / Zinc / Na-pyrithione)[b)]	15103-48-7	2, 6, 7, 9, 10, 13, 21	$PNEC_{Sea\ water}$	5.5
Tralopyril	122454-29-9	21	PNECWater PNECSediment	0.017 6.9

[a)] Cybutrin has now been given an 'unauthorised' status for all product types. Nevertheless, a number of products may still be sold within the sell-off period. In the past, cybutrin was also widely used in treated products, therefore entries may still occur via these applications.
[b)] The metabolite PSA was also selected for the sediment, since accumulations have also been evident in the results of micro- and mesocosm studies.
[*] No specific PNEC values have been derived for these substances, because the transformation products were assessed as being equally or less toxic when compared to the original substances. This is why the PNEC of the original substance has been provisionally listed in this table.

6.4 Work Package 4 – Pollution of groundwater beneath intensively-used agricultural areas on which liquid manure is spread including the pollution of drainage water from these areas

6.4.1 Sample volume

How many measuring points are necessary?

- At least 40 groundwater measuring points
- At least 10 drainage water points, where relevant

How often and at what intervals should measurements be carried out?

- Groundwater: at least 4 times a year (orientation on the management practices of the land areas and the seasons)
- Drainage waters: at least 4 times a year (orientation on the management practices of the land areas (spreading of liquid manure) and on rainfall events)

6.4.2 Sampling points

How are the sampling sites selected?

- Intensively utilised agricultural areas on which liquid manure is spread
- Groundwater measuring point is located on or next to intensively-worked agricultural areas (preferably take samples from near-surface groundwater)
- Coverage of various groundwater catchment areas
- Drained, intensively-worked agricultural areas on which liquid manure is spread
- Measuring points with increased nitrate pollution are recommended (see UBA 2014a[29]) or points at which veterinary pharmaceuticals have been detected during the course of the UBA project, 'Antibiotics and anti-parasitic substances in groundwater beneath locations with a high livestock density' (UBA 2014b)[30]

At which locations should the samples be taken?

- Taking a sample from a groundwater measuring point
- Extraction of the drainage water sample from drainage ditch, or, if appropriate, from the collection system or in the inspection shaft of the drainage system

How should the samples be taken?

- Filter the water phase through suitable filters

Sample methods based on:

- DIN EN ISO 5667-1: 2007 Part 1, Instructions for the preparation of sampling programs and sampling techniques
- DIN 38402-13:1985 Sampling from aquifers
- DIN EN ISO 5667-3: 2013 Part 3, Conservation and handling of water samples

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29 Link to the report: https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/wawi_teil_02_2014_web_korr_25.7.2014_2.pdf

30 Link to the final report: https://www.umweltbundesamt.de/sites/default/files/medien/377/publikationen/texte_27_2014_antibiotika_und_antiparasitika_im_grundwasser_unter_standorten_mit_hoher_viehbesatzdichte_final.pdf

- DIN ISO 5667-14: 2013 Instructions for quality assurance when taking and handling water samples

6.4.3 Analytical requirements

Suitable analytical methods

- GC-MS or HPLC-MS methods in accordance with the substance properties
- Requirements for processes and laboratories are described in the Surface Water Ordinance
- Analysis methods from the EU assessment report on the respective substance can be used where applicable

Availability of isotope-labelled, reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)
- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- It should be noted that biocides which are also used as plant protection product are available as labelled reference substances
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.4.4 Measuring programmes that are possibly relevant

- Monitoring of the chemical status of the groundwater in accordance with the Groundwater Ordinance (GrwV 2010)
- BLAC special measuring programme 'Pharmaceuticals in the Environment' (2003)[31]
- UBA project 'Antibiotics and anti-parasitic substances in groundwater beneath locations with high livestock density' (UBA 2014b)

6.4.5 Prioritised substances

Table 4: Prioritised substances for Work Package 4. TP = Transformation Product.

Substance	CAS no.	Product type[32] pursuant to the Biocidal Products Regulation	Quality parameter [33] in µg/L
Azamethiphos	35575-96-3	18	0.1
Clothianidin (also TP of thiamethoxam)	210880-92-5	8, 18	0.1

31 Link to the final report: http://www.blac.de/servlet/is/2146/P-2b.pdf

32 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

33 Here the quality parameter is the precautionary limit of 0.1 µg/L pursuant to the Groundwater Ordinance (GrwV)

4-fluoro-3-phenoxybenzoic acid (FPB acid, TP of Cyfluthrin)	77279-89-1	18	0.1
Imazalil[a)]	35554-44-0	3	0.1
Imidacloprid	138261-41-3	18	0.1
NOA 407475 (TP of thiamethoxam)		8, 18	0.1
NOA 459602 (TP of thiamethoxam)		8, 18	0.1
Permethrinic acid (DCVA, cis/trans, TP of various pyrethroids, e.g. permethrin, cypermethrin, cyfluthrin)	55701-05-8 59042-49-8 59042-50-1	8, 18	0.1
Prallethrin	103065-19-6	18	0.1
Thiamethoxam	153719-23-4	8, 18	0.1

[a)] Imazalil sorbs on soils robustly, but it also desorbs quickly, therefore its entry into groundwater may be assumed

6.5 Pollution of riverbank filtrate

6.5.1 Sample volume

How many measuring points are necessary?

- At least 15 bodies of water (several wells per water body)

How often and at what intervals should measurements be carried out?

- At least 4 times a year, (spring, summer, autumn, winter)
- If possible, additional sampling during or after extreme hydrological events (long dry periods, high water)

6.5.2 Sampling points

How are the sampling sites selected?

- Urban waters (or water bodies with an increased proportion of wastewater) that are used for drinking water production
- If possible, also consider the waters sampled in Work Packages 1 or 2

At which locations should the samples be taken?

- Taking a sample from a bank filtrate well
- The lowest possible average retention time in the subsurface and a low mixing ratio with groundwater (if known)
- If possible, determination of subsurface retention times and possible mixing ratios with groundwater

How should the samples be taken?

- Filter the water phase through suitable filters

Sample methods based on:

- DIN EN ISO 5667-1: 2007 Instructions for the preparation of sampling programmes and sampling techniques
- DIN 38402-13:1985 Sampling from aquifers
- DIN EN ISO 5667-3: 2013 Part 3, Conservation and handling of water samples
- DIN ISO 5667-14: 2013 Instructions for quality assurance when taking and handling water samples

6.5.3 Analytical requirements

Suitable analytical methods

- GC-MS or HPLC-MS methods in accordance with the substance properties
- Requirements for processes and laboratories are described in the Surface Water Ordinance
- Analysis methods from the EU assessment report on the respective substance can be used where applicable

Availability of isotope-labelled, reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)

- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- It should be noted that biocides which are also used as plant protection product are available as labelled reference substances
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.5.4 Measuring programmes that are possibly relevant

- Monitoring of the chemical status of the groundwater in accordance with the Drinking Water Ordinance (TrinkwV 2011) and Groundwater Ordinance (GrwV 2010)
- BLAC special measuring programme 'Pharmaceuticals in the Environment' (2003)[34]

6.5.5 Prioritised substances

Table 5: Prioritised substances for bank filtrate. TP = Transformation Product.

Substance	CAS no.	Product type[35] pursuant to the Biocidal Products Regulation	Quality parameter[36] in µg/L
2-Aminobenzimidazole (2-AB, TP of carbendazim)	934-32-7	7, 9, 10	0.1
1.2-Benzisothiazolin-3(*2H*)-on (BIT)	2634-33-5	2, 6, 9, 11, 12, 13	0.1
Carbendazim[a)]	10605-21-7	7, 9, 10	0.1
Cybutryne (irgarol)[b)]	28159-98-0	21	0.1
Diclosan (DCPP)	3380-30-1	1, 2, 4	0.1
GS 26575 (TP of cybutryne)[b)]		21	0.1
Imidacloprid[a)]	138261-41-3	18	0.1
Methyl-Diclosan (TP of diclosan)		1, 2, 4	0.1
Octhilinon (Octylisothiazolinone, OIT)	26530-20-1	6, 7, 8, 9, 10, 11, 13	0.1

34 Link to the final report: http://www.blac.de/servlet/is/2146/P-2b.pdf

35 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

36 Here the quality parameter is the precautionary limit of 0.1 µg/L pursuant to the Groundwater Ordinance (GrwV)

Permethrinic acid (DCVA, cis/trans, TP of various pyrethroids, e.g. permethrin, cypermethrin, cyfluthrin)	55701-05-8 59042-49-8 59042-50-1	8, 18	0.1
Prallethrin	103065-19-6	18	0.1
Propiconazol [a)]	60207-90-1	7, 8, 9	0.1
2-pyridine-sulfonic acid (PSA, TP of Na-/Cu-/Zn-Pyrithione)[c)]	15103-48-7	2, 6, 7, 9, 10, 13, 21	0.1
Tebuconazol	107534-96-3	7, 8, 10	0.1
1,2,4-Triazole (TP of propiconazole (among others))	288-88-0	7, 8, 9	0.1
Triclosan[a)d)]	3380-34-5	1[§]	0.1

[a)] Included in Appendix 6 of the OGewV, 2016

[b)] Cybutrin has now been given an ‘unauthorised’ status for all product types. Nevertheless, a number of products may still be sold within the sell-off period. In the past, cybutrin was also widely used in treated products, therefore entries may still occur via these applications.

[c)] Considered to be readily degradable, but there are very many products on the market, so continuous entries into the environment are to be expected.

[d)] Triclosan has now been given an ‘unauthorised’ status for all product types. Nevertheless, a number of products may still be sold within the sell-off period. In the past, triclosan was widely used in treated products, therefore entries may still occur via these applications.

[*] No specific PNEC values have been derived for these substances, because the transformation products were assessed as being equally or less toxic when compared to the original substances. This is why the PNEC of the original substance has been provisionally listed in this table.

[§] The values listed are only provisional, since the assessment report has not yet been finalised.

6.6 Pollution of sewage sludges and (where applicable) contaminated soils, as well as absorption into terrestrial biota

6.6.1 Sample volume

How many measuring points are necessary?

- at least 15 sewage treatment plant sites
- at least 10 soils over which sewage sludge has been regularly spread (soil + terrestrial biota), use of known BDFs

How often and at what intervals should measurements be carried out?

- Sewage sludge sampling:
  - one mixed sample should be taken from the sludge at least 4 times per year (spring, summer, autumn, winter)
- Samples from soil and terrestrial biota
  - when taking samples of soils and terrestrial biota, the procedures should be oriented on the management practice of the areas in question
  - at least twice a year (spring, autumn)

6.6.2 Sampling points

How are the sampling sites selected?

- The sewage treatment plant sites should be selected on the basis of the following points:
  - municipal sewage treatment plant
  - size class (at least 3 different; <10,000 pop., >10,000 to 100,000 pop., >100,000 pop.)
  - development stage (at least stages 3 and 4)
  - sewer system (separate, combined)
  - if possible, this work package should be linked with Work Package 1
- The soils should have been regularly treated with sewage sludge for many years

At which locations should the samples be taken?

- Sewage sludge from the secondary sedimentation basin, if possible use sewage treatment plant sites from Work Package 1
- Take soil and terrestrial biota samples from the centre of the area on which sewage sludge has been spread (representative mixed sample of the topsoil)
- If possible, also take samples from the sewage sludge still to be spread on the agricultural area to be sampled

How should the samples be taken?

Sampling method based on the following:

- Pursuant to the Sewage Sludge Ordinance (AbfKlärV), a mixed sample of five sewage sludge samples is to be used, taken at intervals of several days
- DIN EN ISO 5667-13: 2011 Instructions for the sampling of sludges; one important aspect is the immediate stabilisation of the sludge sample after it has been taken (cooling at 4°C or freezing, alternatively freeze drying)
- Soil: DIN ISO 10381-1: 2003 Part 1: Instructions for setting up sampling programmes
- Soil: DIN ISO 10381-2: 2003 Part 2: Instructions for sampling procedures
- Procedural guidelines for soil sampling have been developed for the ESB. (https://www.umweltprobenbank.de/upb_static/fck/download/SOP_Boden.pdf)

- Procedural guidelines for the sampling of terrestrial biota developed for the ESB (https://www.umweltprobenbank.de/upb_static/fck/download/Regenwurm.pdf)
- VDI 4230-2: 2008 passive bio-monitoring with earthworms as an indicator of accumulations

6.6.3 Analytical requirements

Suitable analytical methods

- GC-MS or HPLC-MS methods in accordance with the characteristics of the target compounds
- Use of fresh sludge samples is preferred
- Other examples of analysis methods in the DBU report: 'Development of a balancing instrument for the entry of pollutants from municipal sewage treatment plants into water bodies' (DBU 2014[37])
- Methods of soil analysis described in literature, e.g. Chitescu et al.(2012): HPLC-MS screening methods for fungicides in soil samples
- Hernández et al. (2013): Simultaneous determination of nine anticoagulant rodenticides in soil through HPLC-MS
- Flores-Ramírez et al. (2012): Analysis methods for fipronil and its degradation products in soil samples
- Analysis methods from the EU assessment report on the respective substance can be used where applicable

Availability of isotope-labelled, reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)
- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- It should be noted that biocides which are also used as plant protection product are available as labelled reference substances
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.6.4 Measuring programmes that are possibly relevant

- Several federal states operate monitoring programmes for sewage sludge, e.g. North Rhine-Westphalia, Bavaria and Baden-Wuerttemberg
- Extended monitoring project for the second survey of emissions, discharges and losses of priority substances for the river basin districts in Germany (financed by the federal states, from 2016) (Federal-State Ad Hoc WG 2016)[38]
- Soil monitoring programmes of the German federal states (Permanent Soil Monitoring Areas)
- ESB (soil samples, earthworms)

[37] Final report: https://www.dbu.de/OPAC/ab/DBU-Abschlussbericht-AZ-29630-01.pdf

[38] Link to the final report on the first survey: http://www.umweltbundesamt.de/publikationen/bestandsaufnahme-der-emissionen-einleitungen

6.6.5 Prioritised substances

Table 6: Prioritised substances for sewage sludge on soils. The substances in the shaded grey lines have been prioritised for both soils/sewage sludge and for terrestrial biota. Substances in the shaded grey lines are only considered to be relevant for soils/sewage sludge. TP = Transformation Product

Substance	**CAS no.**	**Product type[39] pursuant to the Biocidal Products Ordinance**	Quality parameter[40] in µg/kg ww **Type**	**Value**
Alkyldimethylbenzyl ammonium chloride (ADBAC/BKC)[a)]	68424-85-1 68391-01-5 85409-22-9	1, 2, 3, 4, 8, 10, 11, 12, 22	$PNEC_{Soil}$	700
Brodifacoum	56073-10-0	14	$PNEC_{Soil}$	880
Bromadiolon	28772-56-7	14	$PNEC_{Soil}$	8
2-chloro-2- (n-octylcarbamoyl) -1-ethenesulfonic acid (TP of DCOIT)		7, 8, 9, 10, 11, 21	$PNEC_{Soil}$	62*
Cyfluthrin	68359-37-5	18	$PNEC_{Soil}$	2800
Cypermethrin	52315-07-8	8, 18	$PNEC_{Soil}$	100
Cyproconazol[c)]	94361-06-5	8	$PNEC_{Soil}$	20
Deltamethrin	52918-63-5	18	$PNEC_{Soil}$	not known
4,5-Dichloro-2-octyl-2 H-isothiazol-3-on (DCOIT)	64359-81-5	7, 8, 9, 10, 11, 21	$PNEC_{Soil}$	62
Diclosan (DCPP)	3380-30-1	1, 2, 4	$PNEC_{Soil}$	102
Didecyldimethyl ammonium chloride (DDAC)[a)]	68424-95-3 7173-51-5	1, 2, 3, 4, 6, 8, 10, 11, 12	$PNEC_{Soil}$	281
Difenacoum	56073-07-5	14	$PNEC_{Soil}$	55
Difethialon	104653-34-1	14	$PNEC_{Soil}$	890
Imazalil	35554-44-0	3	$PNEC_{Soil}$	950[§]

39 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

40 Quality parameters are the PNEC for soils from the Biocidal Products Regulation implementation procedure.

Methyl-Diclosan (TP of Diclosan)		1, 2, 4	$PNEC_{Soil}$	114
Permethrin	52645-53-1	8, 9, 18	$PNEC_{Soil}$	87.6
Polyhexamethylenbiguanidhydrochloride (PHMB)	27083-27-8	1, 2, 3, 4, 5, 6, 9, 11	$PNEC_{Soil}$	225
Prallethrin	103065-19-6	18	$PNEC_{Soil}$	113
Triclosan[b)]	3380-34-5	1	$PNEC_{Soil}$	115
Na- and Zink-pyrithione	3811-73-2 13463-41-7	2, 6, 7, 9, 10, 21	$PNEC_{Soil}$	150[#]

[a)] Not included in the prioritisation list due to its readily degradable properties, but there are many products on the market, so continuous entries into the environment are to be expected – and the substances also have very strong sorption characteristics.
[b)] Triclosan has now been given an 'unauthorised' status for all product types. Nevertheless, a number of products may still be sold within the sell-off period. In the past, triclosan was also widely used in treated products, therefore entries may still occur via these applications.
[(c)] Not included in the prioritisation list, but already detected in previous sewage sludge studies.

[*]No specific PNEC values have been derived for these substances, because the transformation products were assessed as being equally or less toxic when compared to the original substances. This is why the PNEC of the original substance has been provisionally listed in this table.
[§] The values listed are only provisional, since the assessment report has not yet been finalised.
[#] This value applies to pyrithione.

6.7 Pollution of soils treated with liquid manure and absorption into terrestrial biota, with a targeted study of individual liquid manures where applicable

6.7.1 Sample volume

How many measuring points are necessary?

- at least 30 soils over which sewage sludge has been regularly spread (soil + terrestrial biota), use of known BDFs
- individual liquid manure samples where appropriate, if biocide usage is proven

How often and at what intervals should measurements be carried out?

- Samples from soil and terrestrial biota
  - when taking samples of soils and terrestrial biota, the procedures should be oriented on the management practice of the areas in question
  - at least twice a year (spring, autumn)
- Liquid manure sampling depends on the biocide application

6.7.2 Sampling points

How are the sampling sites selected?

- The soils should have been regularly treated with liquid manure for many years.
- Liquid manure: different animal species, various management systems, proven application of biocides and type of biocide application (e.g. spray application) where applicable.
- In selecting the soils, take the current and past applications of plant protection products into consideration and document these where applicable.

At which locations should the samples be taken?

- Take soil and terrestrial biota samples from the centre of the area on which sewage sludge has been spread (representative mixed sample of the topsoil)
- Take samples of liquid manure from the well-mixed liquids in the tank

How should the samples be taken?

Sampling method based on the following:

- Soil: DIN ISO 10381-1:2003 Part 1: Instructions for setting up sampling programmes
- Soil: DIN ISO 10381-2: 2003 Part 2: Instructions for sampling procedures
- A procedural guideline for soil sampling has been developed within the framework of the ESB (https://www.umweltprobenbank.de/upb_static/fck/download/SOP_Boden.pdf)
- Procedural guidelines for the sampling of terrestrial biota developed for the ESB (https://www.umweltprobenbank.de/upb_static/fck/download/Regenwurm.pdf)
- VDI 4230-2: 2008 Passive bio-monitoring with earthworms as an indicator of accumulations
- EMA/CVMP/ERA/430327/2009: Guideline on determining the fate of veterinary medicinal products in liquid manure (2010)
- UBA project: ‘Development of a test protocol to study the transformation of veterinary pharmaceuticals and biocides in liquid manure’ (UBA 2015b)[41]

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[41] Link to the final report: https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_78_2015_development_of_a_test_protocol_to_study_the_transformation.pdf

6.7.3 Analytical requirements

Suitable analytical methods

- GC-MS or HPLC-MS methods in accordance with the characteristics of the target compounds
- Use of fresh liquid manure samples is preferred
- Methods of soil analysis described in literature, e.g. Chitescu et al.(2012): HPLC-MS screening methods for fungicides in soil samples
- Hernández et al. (2013): Simultaneous determination of nine anticoagulant rodenticides in soil through HPLC-MS
- Flores-Ramírez et al. (2012): Analysis methods for fipronil and its degradation products in soil samples
- Analysis methods from the EU assessment report on the respective substance can be used where applicable

Availability of isotope-labelled, reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)
- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- It should be noted that biocides which are also used as plant protection products are available as labelled reference substances. RON TEST SQL
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.7.4 Measuring programmes that are possibly relevant

- BDFs
- ESB (soil samples, earthworms)

6.7.5 Prioritised substances

Table 7: Prioritised substances for liquid manure/soils/terrestrial biota. The substances in the shaded grey lines have been prioritised for both soils and terrestrial biota; the substances in the shaded green lines are only considered to be relevant for soils. TP = Transformation Product

Substance	CAS no.	Product type[42] pursuant to the Biocidal Products Regulation	Quality parameter[43] in µg/kg ww Type	Value
Alkyldimethylbenzyl ammonium chloride (ADBAC/BKC)[a)]	68424-85-1 68391-01-5 85409-22-9	1, 2, 3, 4, 8, 10, 11, 12, 22	$PNEC_{Soil}$	700
Cyfluthrin	68359-37-5	18	$PNEC_{Soil}$	2800
λ-Cyhalothrin	91465-08-6	18	$PNEC_{Soil}$	2.9
Cypermethrin	52315-07-8	8, 18	$PNEC_{Soil}$	100
Permethrinic acid (DCVA, cis/trans, TP of various pyrethroids, e.g. permethrin, cypermethrin, cyfluthrin)	55701-05-8 59042-49-8 59042-50-1	18	$PNEC_{Soil}$	4600
Deltamethrin	52918-63-5	18	$PNEC_{Soil}$	not known
Didecyldimethyl ammonium chloride (DDAC)[a)]	68424-95-3 7173-51-5	1, 2, 3, 4, 6, 8, 10, 11, 12	$PNEC_{Soil}$	281
Diflubenzuron	35367-38-5	18	$PNEC_{Soil}$	0.33
Hexaflumuron	86479-06-3	18	$PNEC_{Soil}$	0.03
Imazalil	35554-44-0	3	$PNEC_{Soil}$	950[§]
Permethrin	52645-53-1	8, 9, 18	$PNEC_{Soil}$	87.6
Prallethrin	103065-19-6	18	$PNEC_{Soil}$	113
Pyriproxyfen	95737-68-1	18	$PNEC_{Soil}$	1.1

[a)] Not included in the prioritisation list due to its readily degradable properties, but there are many products on the market, so continuous entries into the environment are to be expected – and the substances also have very strong sorption characteristics.

42 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

43 Quality parameters are the PNEC for soils from the Biocidal Products Regulation implementation procedure.

§ The values listed are only provisional, since the assessment report has not yet been finalised.

6.8 Pollution of aquatic biota (limnic ecosystem)

6.8.1 Sample volume

- Fish, molluscs and other invertebrates can be used for screening tests
- Passive monitoring through the sampling of organisms
- Active monitoring by exposing the organisms (e.g. freshwater molluscs) over a defined period of time
- Testing of samples taken at a minimum of 40 sampling points
- Use of archived ESB samples for trend research

Number of individuals and sample volume

- Fish samples: at least 10 individuals of a defined size class per water body (preferably territorial species)
- Mussels: at least 100 individuals (zebra mussels); in absence of zebra mussels, use other indigenous species (e.g. swan mussels)

How often and at what intervals should measurements be carried out?

- Fish monitoring: at least once a year, after the autumnal spawning season
- Mussel monitoring: in the spring and autumn, distribution in the water for around 6 months

6.8.2 Sampling points

How are the sampling sites selected?

- Waters that flow through urban areas or those that are heavily impacted by sewage waters

At which locations should the samples be taken?

- Rivers and lakes (depending on the availability of suitable biota samples and the specific issue or on the selection of analytes)

How should the samples be taken?

- Guidance on the chemical monitoring of sediment and biota, EC 2010; Guidance on biota monitoring, EC 2014)
- Procedural guidelines for the sampling of bream (*Abramis brama*) and zebra mussels (*Dreissena polymorpha*) have been developed for the German ESB.
  http://www.umweltprobenbank.de/upb_static/fck/download/SOP_Brassen.pdf (Brassen);
  http://www.umweltprobenbank.de/upb_static/fck/download/Dreikantmuschel.pdf (Dreikantmuscheln)
- LAWA (2016) LAWA-AO Framework Concept Monitoring Part B, Work Paper IV.3 Conception for biota studies on the monitoring of environmental quality standards pursuant to Directive 2008/105/EC

6.8.3 Analytical requirements

Suitable analytical methods

- GC-MS or HPLC-MS methods in accordance with the characteristics of the target compounds
- Specific methods are available for some biocidal active substances (e.g., triclosan and the transformation product methyltriclosan in fish, Rüdel et al. 2013)
- Analysis methods from the EU assessment report on the respective substance can be used where applicable

Availability of isotope-labelled, reference substances as standards

- Reference substances from CIL, Inc. (www.isotope.com/cil/products/searchproducts.cfm; available in Germany from LGC Standards GmbH, Wesel)
- Dr. Ehrenstorfer (http://www.lgcstandards.com/DE/de/)
- PESTANAL standards from Sigma-Aldrich (http://www.sigmaaldrich.com/analytical-chromatography/analytical-standards.html)
- Standards from Toronto Research Chemicals, available in Germany from BIOZOL Diagnostica Vertrieb GmbH (http://www.biozol.de), Eching
- It should be noted that biocides which are also used as plant protection products are available as labelled reference substances
- Alternative: Use of suitable, isotopically-labelled substances with similar chemical properties, otherwise external calibration with unlabelled standards

6.8.4 Measuring programmes that are possibly relevant

- Surface water monitoring of the federal states pursuant to the Water Framework Directive/Surface Water Ordinance
- Biota monitoring of the federal states in accordance with the Water Framework Directive/Surface Water Ordinance (e.g. fish monitoring and mussel contaminants monitoring in Bavaria)
- German ESB, taking urban-environment sites into consideration (annual sampling of bream and zebra mussels).

6.8.5 Prioritised substances

Table 8: Prioritised substances for aquatic biota. TP = Transformation Product.

Substance	CAS no.	Product Type [44] pursuant to the Biocidal Products Regulation
Bifenthrin[a)]	82657-04-3	8
Brodifacoum[b)]	56073-10-0	14
Carbendazim[c)]	10605-21-7	7, 8, 10
λ-cyhalothrin	91465-08-6	18
Cypermethrin	52315-07-8	8, 18
Deltamethrin	52918-63-5	18
Difenacoum	56073-07-5	14
Difethialon[b)]	104653-34-1	14
Etofenprox[d)]	80844-07-1	8, 18
Flocoumafen	90035-08-8	14

44 Product types in which the respective active biocidal substance is used; see Appendix 2 for description

Imazalil	35554-44-0	3
Methyl-diclosan (TP of diclosan)	-	1, 2, 4
Methyltriclosan (TP of triclosan)[e)]	4640-01-1	1
Permethrin	52645-53-1	8, 9, 18
d-phenothrin[f)]	26046-85-5	18
Prallethrin	103065-19-6	18
Pyriproxifen	95737-68-1	18
Triclosan[e)]	3380-34-5	1

[a)] Widely-used insecticide of the pyrethroid group. This is a potential PBT substance – there is reason to suspect that it also has endocrine-disrupting properties.
[b)] PBT substance, already found in fish during preliminary testing; entries of this substance into surface water are therefore likely.
[c)] Included in Appendix 6 of the OGewV, 2016; the substance is persistent in water and there is reason to suspect that it also has endocrine-disrupting properties
[d)] The substance is classified as bio-accumulative and has already been detected in surface waters.
[e)] Triclosan has now been given an 'unauthorised' status for all product types. Nevertheless, a number of products may still be sold within the sell-off period. In the past, triclosan was also widely used in treated products, therefore entries may still occur via these applications.
[f)] Widely-used insecticide of the pyrethroid group; it is deemed to be a potential PBT substance.

[*] No specific PNEC values have been derived for these substances, because the transformation products were assessed as being equally or less toxic when compared to the original substances. This is why the PNEC of the original substance has been provisionally listed in this table.
[§] The values listed are only provisional, since the assessment report has not yet been finalised.

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Appendix 1: Prioritisation concept

The evaluation described in table 9 is carried out for each substance per work package.

Table 9: Prioritisation concept for the monitoring of biocides.

Step 1: Estimated quantity emitted[45]	
Number of emission-relevant product types (PTs[46]), in which the substance is used	
▶ Emission-relevant PTs: 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 14, 16, 18, 19, 21	
▶ 1 point per PT	
▶ Maximum of 3 points	
Number of products with the active substance registered with the BAuA (German Federal Institute for Occupational Safety and Health)[47]	
▶ <=10	→ 0 points
▶ 11-100	→ 1 point
▶ 101-1000	→ 2 points
▶ >1000	→ 3 points
EU production or import quantity of substances registered in the context of REACH, if published[48]	
▶ Not LPV/HPV (<10 tons per year)	→ 0 points
▶ LPV (10-1000 tons per year)	→ 2 points
▶ HPV (>1000 tons per year)	→ 3 points
▶ Unknown	→ 1 point
Emissions score: Points total for the 3 criteria	
Step 2: Eco-toxicological effects	
Amount of PNEC for aquatic organisms [µg/L]	
▶ Unknown	→ 1 point
▶ <0.01	→ 4 points
▶ <=0.1	→ 3 points
▶ <=1	→ 2 points
▶ <=10	→ 1 point
▶ >10	→ 0 points
Fulfilment of the T criterion (toxicity) [49]	
▶ Unknown	→ 1 point
▶ Yes	→ 3 points
▶ Potential	→ 2 points
▶ No	→ 0 points
Bio-accumulation behaviour	
Based on the bio-concentration factor (BCF)	
▶ Unknown	→ 1 point
▶ <=100	→ 0 points
▶ >100	→ 1 point
▶ >2000	→ 2 points
▶ >5000	→ 3 points

45 Here the same entries are made for metabolites and the original substances.

46 See Appendix 2 for a description

47 All biocide products marketed in Germany must be registered in accordance with the German Biocide Reporting Ordinance (link: http://www.baua.de/de/Chemikaliengesetz-Biozidverfahren/Biozide/Produkt/Meldeverordnung.html)

48 Link to the ECHA database: http://echa.europa.eu/de/information-on-chemicals/registered-substances

49 Criteria are defined in Annex XIII of the REACH Regulation (Regulation (EC) 1907/2006); if an original substance has been classified as T, the metabolite is considered to be a 'potential' T, even if no specific data is available.

Suspected endocrine-disruptive properties [50]	
▶ Unknown	→ 1 point
▶ Yes, or potential	→ 2 points
▶ No	→ 0 points
Effects score: Points total for the 4 criteria	
Step 3: Entry into and behaviour in the affected environmental compartment	
No. of product types (PTs[51]) in which the substance is used and which are emission-relevant for a work package[52]	
▶ For the relevant PTs, see the work package-specific parameters	
▶ 1 point per PT	
▶ Maximum of 3 points	
Bio-degradability [53]	
▶ Unknown	→ 1 point
▶ Readily bio-degradable	→ 0 points
▶ Not readily bio-degradable	→ 2 points
Fulfilment of the P criterion (persistence) [54]	
▶ No	→ 0 points
▶ Potential	→ 1 point
▶ P	→ 2 points
▶ vP	→ 3 points
Entry/behaviour score in environmental compartment: Points total for the 3 criteria	
Priority = the product of the respective scores for emissions, effects and entry/behaviour in the environmental compartment	

50 Evaluation is carried out according to transition criteria for substances with endocrine-disruptive properties, see Biocidal Products Regulation, Art. 5

51 See Appendix 2 for a description

52 Here the same entries are made for metabolites and the original substances.

53 If a metabolite is classified as P, its bio-degradability is assessed as being 'not readily bio-degradable', even if no specific test is available.

54 Criteria are defined in Appendix XIII of the REACH Regulation

The relevant substances for a work package are filtered from the entire pool of substances, based on work-package-specific parameters.

Work package-specific parameters
WP 1: Sewage treatment plant – Surface water ▶ Relevant PTs*: 1, 2, 3, 4, 6, 7, 9, 10, 11, 12, 14, 18, 19 ▶ Not readily bio-degradable ▶ Half-time hydrolysis ≥ 48 hours (12°C) ▶ Half-time in the water sediment system ≥ 48 hours (12°C) ▶ Koc[#] < 5000 For the sediment in addition ▶ Koc[#] ≥ 1000
WP 2: Rainwater – Surface water ▶ Relevant PTs*: 2, 6, 7, 8, 9, 10, 14, 18 ▶ Not readily bio-degradable ▶ Half-time hydrolysis ≥ 48 hours (12°C) ▶ Half-time in the water sediment system ≥ 48 hours (12°C) For the sediment in addition ▶ Koc[#] ≥ 1000
WP 3: Direct entries into surface waters ▶ Relevant PTs*: 21 ▶ Not readily bio-degradable ▶ Half-time hydrolysis ≥ 48 hours (12°C) ▶ Half-time in the water sediment system ≥ 48 hours (12°C) For the sediment in addition ▶ Koc[#] ≥ 1000
WP 4: Groundwater below agricultural areas ▶ Relevant PTs*: 3, 18 ▶ Not readily bio-degradable ▶ GUS[§] ≥ 2.8 (if GUS cannot be calculated, use value of 3.0)
River bank filtrate ▶ Relevant PTs*: 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 14, 18, 19, 21 ▶ Not readily bio-degradable ▶ Half-time hydrolysis ≥ 48 hours (12°C) ▶ Half-time in the water sediment system ≥ 48 hours (12°C) ▶ Koc[#] < 5000
Sewage sludges – soils, terrestrial biota ▶ Relevant PTs*: 1, 2, 3, 4, 6, 7, 9, 10, 11, 12, 14, 18, 19 ▶ Not readily bio-degradable ▶ Half-time hydrolysis ≥ 48 hours (12°C) ▶ Koc[#] ≥ 1000 Instead of Koc ≥ 1000 for terrestrial biota ▶ BCF (fish) ≥ 500 ▶ Risk of secondary poisoning (terrestrial)
Soils over which liquid manure has been spread, terrestrial biota ▶ Relevant PTs*: 3, 18 ▶ Not readily bio-degradable ▶ Half-time hydrolysis ≥ 48 hours (12°C) ▶ Koc[#] ≥ 1000 Instead of Koc ≥ 1000 for terrestrial biota ▶ BCF (fish) ≥ 500 ▶ Risk of secondary poisoning (terrestrial)

Aquatic biota
► Relevant PTs*: 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 14, 18, 19, 21 ► Not readily bio-degradable ► Half-time hydrolysis ≥ 48 hours (12°C) ► BCF (fish) ≥ 500 ► Risk of secondary poisoning (aquatic)
Direct entries into soils
► Relevant PTs*: 2, 6, 7, 8, 9, 10, 14, 18, 21 ► Not readily bio-degradable ► Half-time hydrolysis ≥ 48 hours (12°C) ► Koc[#] ≥ 1000 Instead of Koc ≥ 1000 for terrestrial biota ► BCF (fish) ≥ 500 ► Risk of secondary poisoning (terrestrial)

#Koc = distribution coefficient of water-organic substance;

* see Appendix 2;

[§] GUS: Groundwater Ubiquity Score; GUS = log(half-time in soil, 12°C) × (4 - log(KOC))

Appendix 2: Biocidal product types

Table 10: Overview of the 4 main groups (MGs) and the 22 product types (PTs) pursuant to Biocidal Products Regulation EU 528/2012

No.	Description
MG 1	**Disinfectants**
PT 1	Human hygiene
PT 2	Disinfectants and algaecides not intended for direct application to humans or animals
PT 3	Veterinary hygiene
PT 4	Food and feed area
PT 5	Drinking water
MG 2	**Preservatives**
PT 6	Preservatives for products during storage
PT 7	Film preservatives
PT 8	Wood preservative
PT 9	Fibre, leather, rubber and polymerised materials preservatives
PT 10	Construction material preservatives
PT 11	Preservatives for liquid-cooling and processing systems
PT 12	Slimicides
PT 13	Working or cutting fluid preservatives
MG 3	**Pest control**
PT 14	Rodenticides
PT 15	Avicides[§]
PT 16	Molluscicides, vermicides and products to control other invertebrates
PT 17	Piscicides[§]
PT 18	Insecticides, acaricides and products to control other arthropods
PT 19	Repellents and attractants
PT 20	Control of other vertebrate[§]
MG 4	**Other biocidal products**
PT 21	Antifouling products
PT 22	Embalming and taxidermist fluids

[§] These product types cannot be authorised in Germany, pursuant to § 4 of the Biocidal Authorisation Ordinance (ChemBiozidZulV)