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Thematic Strategy on Sustainable Use of Plant Protection Products – Prospects and Requirements for Transferring Proposals for Plant Protection Products to Biocides

Annex I:
Occurrence and impact of biocides in the environment
- Results of the Literature Research

Stefan Gartiser (project direction) [1)]
Heike Lüskow [2)]
Rita Groß [3)]

[1)] Hydrotox GmbH, D-79111 Freiburg
[2)] Ökopol GmbH, D-22765 Hamburg
[3)] Öko-Institut e.V., D-79100 Freiburg

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Contents

0 Introduction

Biocides are intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means (Article 2 (a) 98/8/EC). Due to these properties biocides pose potential hazards and risks to human health and the environment. The discussion on the effects of biocides began with a focus on human health impacts. The scandals surrounding the use of certain wood preservatives in the 70s and 80s as well as the discussion on pyrethroides for textile finishing and insect control in private households resulted in pressure for greater regulatory control of this sector. Consequently, active substances such as Pentachlorophenol and Lindane were removed from the market.

With regard to environmental impacts, concerns about the use of antifouling agents as ship hull coatings began to be debated in the early 1980s. In particular, the high ecotoxicity and endocrine effects of tributyltin compounds (e.g. the so-called imposex effects on snails) has resulted in a worldwide ban of these compounds.

Concerning the emission of biocides to the environment only limited reliable information is available to date and biocides are rarely considered in monitoring programmes. It is known that there are direct emissions to the environment (e.g. from cooling water biocides, swimming pool water, masonry preservatives, and antifouling agents). The majority of biocidal emissions are indirectly released via municipal sewage treatment plants (STP). Thus, for the risk assessment of biocides understanding their behaviour in STP (biodegradation, adsorption, and volatilisation) is a principle concern. However, risk assessment must also address the discharge of about 3-10% of the wastewater volume without treatment through the storm water overflow of the STP.

Given the known concerns, a systematic internet search and review of the literature on the occurrence and impacts of biocides in environmental media has been carried out. The object of this exercise was to identify problems which should be addressed when establishing measures on sustainable use of biocides. The results are presented in this Annex.

1 Data sources

Much information on the use of pesticides and to a lesser extent of biocides can be found in publicly available sources. The European Commission provides detailed information about the revision of the Biocidal Product Directive[1], the Thematic Strategy on Sustainable Use of Pesticides[2] and the revision of the Plant Protection Products Directive[3], including research projects, impact assessment studies, Emission Scenario Documents (ESDs)[4], workshops and stakeholder consultation protocols. The assessment reports of active substances included in Annex I or IA are available from the European Chemical Substances Information System (ESIS) and may contain some relevant information on sustainable use (e.g. data used for the exposure and environmental fate assessment, and recommendations about environmental protection measures)[5]. However, a systematic evaluation of all these data would go beyond the objectives and time budget of this study. Additionally, the contractors have direct access to discussion documents and meeting protocols from the competent authorities provided to them by the CIRCA Interest Group on Biocides. These documents are available to Competent Authorities and observers who have indicated a substantial interest in being kept informed.

In January 2009 a draft report of a study providing an "Assessment of different options to address risks from the use phase of biocides" was distributed (COWI, 2009). In addition, an assessment of the antibiotic resistance effects of biocides has recently been carried out by the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR, 2009).

The German Competent Authorities have initiated several research projects related to the implementation of the Biocidal Product Directive (ULIDAT data source, http://doku.uba.de/).

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1 http://ec.europa.eu/environment/biocides/revision.htm

2 http://ec.europa.eu/environment/ppps/home.htm

3 http://ec.europa.eu/food/plant/protection/evaluation/index_en.htm, http://www.efsa.europa.eu/EFSA/KeyTopics/efsa_locale-1178620753812_Pesticides.htm

4 http://ecb.jrc.ec.europa.eu/biocides/

5 http://ecb.jrc.ec.europa.eu/esis/

The German Federal Institute for Occupational Safety and Health (FIOSH) funded several research projects about occupational exposure to biocides (e.g. wood preservatives, insecticides, antifouling agents) which also provide useful information about the mode of application and resultant potential emissions to the environment (Bleck et al., 2008; Schneider et al., 2008).

A preliminary literature search was carried out using the databases Science Direct (www.sciencedirect.com), Medline (http://www.ncbi.nlm.nih.gov/sites/entrez), and ULIDAT ((http://doku.uba.de/), covering the period from 2000 to 2008. In addition, information was gathered from the websites of universities known to be involved in environmental research (e.g. the University of Frankfurt, http://www.bio.uni-frankfurt.de/ee/ecotox/publications/).

Monitoring data are available from river management organisations and water suppliers. The following websites have been consulted:

River Water Companies (RIWA)	http://www.riwa-rijn.org/riwa_en.html
International Association of Waterworks in the Rhine catchment area (AWR)	http://www.iawr.org
Internationale Kommission zum Schutz des Rheins (IKSR)	http://www.iksr.org
International Commission for the Protection of the Danube River (ICPDR)	www.icpdr.org
International Commission for the Protection of the Elbe River (ICPER)	www.ikse-mkol.org

The evaluation of monitoring data was limited to European water bodies.

2 Quantitative data and indicators for sustainable use

Statistical information on the volume and value of the pesticides market provided by EUROSTAT (and the “Statistische Bundesamt”) generally do not distinguish between biocide and plant protection active substances. Rough estimates of the biocides market from several sources suggest that about 25% of the total pesticides market can be attributed to biocides (Gartiser et al., 2007). Some consumption estimates (disinfectants in hospitals, biocides in cooling water, disinfectants/bleaching agents/-preservatives in household cleaning products) are available from several research projects funded by the German Environmental Agency (Kahle et al. 2009). Further-more, data on pest control biocides applied in private homes have been provided by industry associations. In 2007 the Industrie Verband Agrar (IVA) member companies sold about 20 t of pest control biocidal actives (mainly PT 18/19), 3 t of ant control actives and 10 t of rodenticidal actives (IVA, 2008). However, no data on specific active substances are available from this source.

The most detailed study on biocide consumption available in Europe is the Danish inventory of biocides which is based on information from the Danish Pesticide Statistics, the database of the Danish Product register, trade organisations, private companies, Statistics Denmark, and research institutions. In total 3,600 - 5,530 t of biocidal active substances were consumed in Denmark in 1998 (Lassen et al., 2001).

The Finnish register of chemical products (KETU) and the Nordic Substance Data-base have been used to establish a priority list of 77 chemicals including industrial chemicals, biocides and pesticides. For 17 priority biocides the use pattern, number of products and sales in 1999 have been assessed, Five of which (creosote oil, D-limone, hexachloroethane, naphthalene, and 1,4-dichlorobenzene) are also used as industrial chemicals. Two biocidal active substances (permethrin and deltamethrin) are used as agricultural pesticides, and one metal (copper) is used as biocide in disinfectants and wood preservatives. The biocides used in the greatest quantities were PAHs in Creosote oil (544 t per year), followed by the Phoxim used as insecticide and wood preservative (479 kg per year), and the insecticide Deltamethrin (301 kg per year). The consumption of the rodenticides Bromadiolone, Difenacoum and Brodifacoum was up to 7 kg per year (Koivisto 2001).

Among the scarce information available, the BIOMIK study on quaternary ammonium compounds calculated that the total consumption of alkylbenzyldimethylammonium-chloride (BAC) in Switzerland from biocidal applications was 90 t/a, and of dialkyldimethylammoniumchloride (DDAC) 30 t/a (Morf et al., 2007; Buser et al., 2009). Approximately, 11 t/a of BAC and DDAC are emitted to the environment (5 t/a to the aquatic environment) with the majority of BAC and DDAC emissions (>90%) being attributed to non-biocidal diffuse sources. In addition, data from Sweden show that about 77% of BAC consumption and 87% of DDAC are for non-biocidal purposes. The contribution of emissions from WWTPs (point source emissions) to the environment is only about one tenth of other emissions, and thus relatively low, compared to diffuse emissions (Morf et al., 2007; Buser et al., 2009).

It should be noted that while establishing the BPD there were proposals that the applicants should be required to report the amount of active substances produced. Furthermore, in the common core data set for active substances, the “likely tonnage to be placed on the market per year” is to be indicated (Annex IIA, 5.8). These data are confidential and are often not reported by applicants. However, an overall evaluation of existing data provided by the Commission has been carried out within the study “Assessment of different options to address risks from the use phase of biocides” (COWI, 2009). Here, an absolute minimum estimate of 400,000 t active substances production in the EU has been calculated.[6] Interestingly, within the majority of PTs relatively few substances (< 5) constitute significantly more than 50% of the total production/import tonnage registered. The manufacturing/import of substances for use as general disinfectants accounted for almost two thirds of the total tonnages for all 23 PTs while other PTs - especially 14, 15, 16, 17, 22 and 23 - are produced/imported in very low tonnages (< 25 t/a).

With regard to plant protection products, an EU regulation will soon provide for the gathering of statistics on the marketing and use of these products. Member States will be obliged to provide detailed statistics on sales, distribution and use. These data are intended to provide reliable data and indicators of the progress of improvements

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6 The order of magnitude of this estimate is quite well confirmed by extrapolating consumption data of the most comprehensive study on biocide consumption available for Denmark (Lassen et al. 2001). Here, total consumption of biocidal active substances was calculated as being 3,600 to 5,530 t/a. Comparing the population of Denmark (5.4 million) with that of the EU-27 (493 million) total consumption of biocides in the EU-27 can be extrapolated as being 329,000 to 505,000 t/a. However, the relative distribution of biocide tonnage on product types at EU level and in Denmark varies considerably.

resulting from the Thematic Strategy on Sustainable Use. The draft regulation concerning statistics on plant protection products includes reporting obligations for suppliers concerning the plant protection products that they place on the market. In addition, professional users will be required to keep records on the use of plant protection products in relevant areas (COM (2006) 778 final).

A reduction in the number of incidences of animals and humans being poisoned by biocidal products might be another indicator for sustainable use of biocides. Member States are obliged to collect information on such incidents in accordance with Article 23 of the BPD. These data are collected by the Commission and summarised in the composite reports (European Commission, 2008). However, only 16 out of 26 Member States have thus far submitted data, Germany being among those that have not submitted data. In total 15 539 cases of poisoning/exposure to active substances have been reported from 2003 to 2006 but in most cases it is not clear whether these are linked to biocidal products, plant protection products, detergents, or products containing dangerous chemical substances in general. Nevertheless, it was possible to note that the majority of these poisonings are related to the professional or household use of insecticides, rodenticides, disinfectants, repellents and wood preservatives. The active substances most frequently responsible for these incidents are Bromadiolone, Difenacoum, Permethrin, Alphachloralose, sodium hypochlorite, organophosphates, and carbamates (European Commission, 2008).

In Germany, the Federal Institute for Risk Assessment (BfR) is responsible for the evaluation cases of poisoning. In 2006, 6 cases of poisoning with wood presser-vatives, 4 cases with rodenticides and 30 cases with insecticides were reported. However, no unambiguous distinction is made between plant protection products and biocides; neither is there systematic collection of information on cases involving wildlife or domestic animals.

A research project funded by the German Environmental Agency investigated potential malpractice during the use phase of plant protection products, finding a high incidence of malpractice, especially during the application of plant protection products (Umweltbundesamt, 2006). In comparison, very little information has been collected on the details of malpractice during biocide application. However, for some PTs (PT 8, 18, 21) malpractice is documented in research projects of the German Federal

Institute for Occupational Safety and Health (BAuA), where the focus was on occupational exposure with no consideration of emissions to the environment.

3 Emissions to the environment

3.1 Emission routes

The COWI study from 2009 gives a qualitative overview of main emission routes for biocides and distinguishes between exposure to the environment during the application and the service-life phases. Disinfectants of PT 1, PT 2 and PT 4 are mainly discharged to municipal wastewater treatment plants (WWTPs) while disinfectants of PT 3 can also be emitted to soils or surface water with direct exposure of the environment in the use phase of biocides considered to be most significant for PT 7, PT 8, PT 10, PT 18 and PT 21. Direct non-target exposure of biota is mainly from the use of PT 14-19 and PT 23 (COWI, 2009). Cooling water biocides (PT 11) are emitted directly to surface water and indirectly discharged to WWTPs. Also slimicides (PT 12) and metal working fluids (PT 13) are mainly discharged to WWTPs, and waste disposal is considered to be the main emission route for embalming and taxidermist fluids (PT 22).

The SCENIHR study on the assessment of the antibiotic resistance effects of biocides identified the following applications as having emissions to the environment: disinfection of the outflow of WWTPs, cooling towers, antifouling agents, building materials, and antimicrobial surfaces (SCENIHR, 2009).

A literature survey on the occurrence of micro-pollutants, such as pesticides in municipal wastewater, and rough estimates of removal efficiency from physical sorption and vocalization parameters has been documented by van Beelen (2007). However, most pesticides mentioned belong to the chemical class of herbicides, such as Glyphosate (CAS 1071-83-6) or Mecoprop (CAS 93-65-2) which are not included in the Review Programme for biocides. The insect repellent Dietyltoluamide (DEET), which is regularly reported in WWTP effluents and surface water, was included in this analysis.

The sorption of organic substances on activated sludge plays an important role for removal efficiency. Substances with an octanol-water partition coefficient (log P_{OW}) below 2.5 are predicted to have low sorption potential with the consequence that, if they are not biodegradable, they will be released into surface water. In a review study on pollutants in urban wastewater and sewage sludge only a few biocides were included, notably Triclosan (Thornton et al., 2001).

The concentrations of pesticides (plant protection products and biocides) in the discharge to municipal sewage treatment plants and their elimination during the treatment was analysed by Singer et al. (2010, see table 1).

Table 1: Elimination of biocides in Sewage treatment plants

	Biocide or PPP *)	Primary effluent [ng/L]	Elimination [%]
Carbendazim	B, P (fungicide)	110 ± 30	36 ± 23
Diazinon	B (insecticide)	60 ± 10	48 ± 20
Diuron	B (herbicide)	60 ± 30	44 ± 47
Irgarol 1051	B (bactericide)	10 ± 4	52 ± 36
Isoproturon	B (herbicide)	90 ± 100	63 ± 36
Mecoprop	P (herbicide)	870 ± 590	-11 ± 109
Terbutryn	B (herbicide)	70 ± 20	72 ± 14

Data from Singer et al. (2010)
*) Diazonon, Diuron and Terbutryn formerly have been approved PPP

The results demonstrate that many biocides are not completely removed during wastewater treatment. Average eliminations may well be low, and usually below 50%, except for Isoproturon (mean elimination 63%) and Terbutryn (72%). Treated wastewater was identified as the major exposure route of the urban use biocides to the receiving river, although by-pass sewer overflows of untreated wastewater during rain events were also important. In the final effluent, Mecoprop was identified in the highest concentrations, with concentrations of 1-2 orders of magnitude higher than for other biocides and pesticides. For this active substance, the average concentrations in surface water ranged from below the limit of quantification (LOQ) to 520 ng/L. However, only the concentrations of Diazinon downstream the WWTP (20 ± 8.0 ng/L) were above the relevant threshold value for chronic effects of 3 ng/L (Singer et al. 2010).

Other studies also confirm that WWTPs are an important emission source for pesticides to surface water. In Switzerland about 20% of the total load of pesticides in surface water has been attributed to emission from WWTPs (Hanke et al., 2007). A systematic analysis of the importance of different emission sources of Pyrethroide insecticide to surface water (Sacramento-San Joaquin River, USA) revealed, that Pyrethroids passed through secondary treatment systems at municipal wastewater treatment facilities and were commonly found in the final effluent. Agricultural discharges in the study area only occasionally contained pyrethroids while discharges of the pyrethroid bifenthrin via urban storm water runoff was sufficient to cause water column toxicity in two urban streams when applying the amphipod, *Hyalella azteca* as test organism with 96 h exposure time. The maximum concentrations from the outflow of WWTP were as follows: Bifenthrin (29.8 ng/L), Cyfluthrin (17.8 ng/L), Cypermethrin (12.3 ng/L), Deltamethrin (3.5, ng/L), Esfenvalerate (4.3 ng/L), Fenpropathrin (6.1 ng/L) Lambda-cyhalothrin (6.2 ng/L), and Permethrin (45.8 ng/L) (Weston et al. 2010).

3.2 Monitoring substances of concern

With the exception of antifouling agents, monitoring data for biocides in the aquatic environment are currently very limited, with far more monitoring data available for other chemical categories such as plant protection products and pharmaceuticals. Available data are presented in chapter 4.2.3.

<u>Identification of main emission sources:</u>

One general problem of monitoring is the fact that chemical analyses do not distinguish between different sources of emissions to the environment, with many active substances being used both in plant protection and biocidal products. Furthermore, many chemicals such as food or cosmetic preservatives, bleaching agents, pharmaceuticals, and water treatment chemicals are also used as biocides (dual or multiple use). The main emission source is not always known and thus the contribution from biocidal uses alone is difficult to assess.

There is considerable overlap between biocidal and plant protection active substances. In this respect, a systematic analysis has revealed that 58 biocidal active substances within the Review Programme are also used in plant protection products, among them many insecticides (Annex 1). However, the contribution of biocides to the overall load of these actives is not known.

Another example of dual use is 2-Mercaptobenzothiazole (Benzothiazole-2-thiol CAS 149-30-4), which is a biocidal active substance (PT 2, 7, 9, 11-13) but which has its major use is as a vulcanization accelerator within the rubber industry. 2-Mercaptobenzothiazole has been identified as an environmental pollutant but has also been shown to be biodegradable (Gaja et al., 1997).

In a German study, the emission sources and pathways of copper, zinc and lead to water and soil were analysed, identifying traffic (vehicles), the building sector, water supply and other specific sources (e.g. galvanized products) as the main emission sources. In this respect, the contribution of copper and zinc containing biocides[7] was considered to be of minor importance (Hillenbrand et al., 2005). Recently, the application of copper as a plant protection product has been questioned and restricted by authorities for environmental reasons, especially for ecological viniculture, pomiculture and cultivation of other crops (Kühne et al., 2008).

A further example is sodium dimethyldithiocarbamate (CAS 128-04-1) which is a biocidal active substance supported for PT 9-12, a plant protection product and is also used as a wastewater treatment chemical for metal precipitation in presence of complexing agents. These organosulfides were identified as a source of algae ecotoxicity after biological treatment of wastewater from metal surface treatment industries (Gartiser et al., 2008). Dithiocarbamates, used as fungicides, herbicides, and as chelating agents to remove metals from industrial wastewater, have been reported to be contaminated with N-Nitrosodimethylamine (NDMA), a potential drinking water carcinogen (Mitch et al., 2003).

To summarise: attempts to combine the contributions of different emission sources from the uses of active substances covered by different regulatory regimes have identified high levels of uncertainty regarding the main areas of application relevant for environmental exposure. However, the concentration patterns for different compounds in surface water may identify the relevant sources of exposure. Within a study on the pesticide dynamics in surface water Wittmer et al. (2010) distinguished five types of concentration patterns:

a) compounds that showed elevated background concentrations throughout the year (e.g. diazinon >50 ng /L), indicating a constant household source;
b) compounds that showed elevated concentrations driven by rain events throughout the year (e.g. diuron 100–300 ng/L), indicating a constant urban outdoor source such as facades;

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[7] Examples are copper (PT 2, 4, 5, 11, 21), copper sulphate (PT 1, 2, 4), copper thiocyanate and dicopper oxide (both PT 21) as well as copper oxide and copper dihydroxide (both PT 8) and Zinc sulphide (PT 7, 9, 10).

c) compounds with seasonal peak concentrations driven by rain events from urban and agricultural areas (e.g. mecoprop 1600 ng/Land atrazine 2500 ng/L respectively);
d) compounds that showed unpredictably sharp peaks (e.g. atrazine 10,000 ng/L, diazinon 2500 ng/L), which were most probably due to improper handling or incorrect disposal of products; and finally,
e) compounds that were used in high amounts but were not detected in surface waters (e.g. isothiazolinones)

Among the substances included in the study the herbicides Isoproturon, Diazinon, Diuron, Terbtryn and the fungicide Carbendazim and 3-iodo-2-propynyl-butyl-carbamate also have a biocidal use (or dual use together with plant protection products) while Atrazine and Mecoprop are exclusively used for plant protection purposes.[8] A survey on the quantities of plant protection products used by farmers revealed the following order of consumption: Isoproturone > Glyphosate, Atrazin, and Terbuthylazin. Only minor amounts of other active substances such as Mecoprop and Diazinon had been used for plant protection purposes. Furthermore, flat roofs with bitumen felts treated with Mecoprop have been identified as the main source of this herbicide (Wittmer 2009).

The Swedish Environmental Protection Agency initiated a study concerning the emission, distribution and exposure of some major biocides. The study concluded that biocides do not seem to constitute a major problem in the Swedish environment. Even where some of these are frequently used close to important emission sources, the levels are usually well below risk levels. These results are probably due to a combination of low amounts used in relation to the size of the environmental compartments they are emitted to, and a generally high degree of (bio)degradability (Törneman et al. 2008, see table 2). In a previous monitoring study on biocides, including Bronopol, 4-Chloro-3-cresol, 2-Mercaptobenzothiazole, N-Didecyldimethyl-ammoniumchloride (DDMAC), Propinconazol, Resorcinol, 2-Thiocyanomethyl-thiobenzothiazol, Triclosan and several parabens, similar conclusions were drawn (Remberger et al. 2005).

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[8] The concentration pattern for Mecoprop resembled on that of Diuron. The authors concluded that this would be an indication of constant sources from urban losses, most likely from building materials (facades, roofs). In this case this would have to be attributed to old sources because Mecoprop is not supported in the review programme for existing biocidal actives.

Table 2: Consumption of biocides and monitoring data in Sweden

Active substance consumption in Sweden	Main sources	Monitoring data
Tolylfluanide 143 [t/a]	Very common fungicide in a number of paint and wood oil products. All permits for agricultural use have been revoked.	Paint industry: Sediments of storm water manholes 0,26 - 0,85 mg/kg, Storage site for treated wood: Soil 0,3 mg/kg Not detected in the storm water, groundwater, untreated waste water, sludge from waste water treatment or soil samples collected at paint industries.
Chlorothalonil 1.3 [t/a]	Wood preservation products and, in other countries, boat paints. All permits for agricultural use have been revoked.	Not detected in any samples (limit of quantification in water 0.01 – 10 µg/L in soils and sediments 0.01 – 0.1 mg/kg). Has not been found within the Swedish regional aquatic monitoring of pesticides.
Diuron 6.8 [t/a]	Use as weed killer on railway embankments, roads, parking lots etc. (now discontinued). Main usage as a biocide in water based paints for exterior use and boat paints. Also included as a biocide in glues and lacquers used in the engineering industries.	Landfill leachate: 0.05 - 0.09 µg/L. Paint industry: Storm water 0.05 - 0.21 µg/L, groundwater 0.06 - 0.4 µg/L, inlet waste water treatment plant 32 µg/L. Storage for treated wood: Storm water sediment 0.0188 mg/kg. Background lake: Sediment 0.086 mg/kg. Regional monitoring of pesticides: Found in 0.2-1% of samples (median in surface water 0.0485 µg/l).
Cypermethrin 0.8 [t/a]	Insecticide for forestry uses (increased after storms when a large number of tress had to be stored). Also, biocidal use to combat and control ants in gardens and inside buildings.	Topsoil in proximity to storage sites for timber: 0.15 and 0.39 mg/kg. Storm water from detached houses: 0.1 and 0.45 µg/l. Not found in surface waters, ground waters and drinking waters.
Propiconazole 20 [t/a]	Fungicide in cereal crops and grass seed cultivations (e.g. golf courses) and paint and wood oil products for exterior use.	Paint industry: Storm water 0.67 - 85 µg/L, groundwater 0.28 - 7.9 µg/L, storm water manhole sediments 0.22 - 2.5 mg/kg, inlet waste water treatment plant 150 µg/L., sludge of waste water treatment plant 23 mg/kg. Storage for treated wood: Storm water manhole sediments 0.12 - 0.48 mg/kg, storm water 2.1 µg/L, soil 0.32 mg/kg. Regional monitoring of pesticides: Surface water 0.03 µg/l (median), 1 µg/l (maximum).
Kathon 25 [t/a]	Mixture of 2-methyl-3-isothiazolinone and 5-chloro-2-methyl-3-isothiazolinone. Preservatives used in aqueous-based industrial products (cleaning agents, cosmetics, toiletries, household products) as well as slimicides used in pulp and paper industries.	Not detected in any samples (limit of quantification in water 1 – 100 µg/L, in soils and sediments 0.05 – 0.1 mg/kg. German data suggest that isothiazolinone compounds were not found in effluent waters from the municipal wastewater treatment plants (Rafoth et al. 2007).

Data from Törneman et al. (2008)

Comparison with existing list of priority substances:

Annex X of the Water Framework Directive 2000/60/EC identifies priority substances for which a progressive reduction of emissions to water is intended. Among them are several biocides which a) are supported for Annex I inclusion (Isoproturon (PT 7, 9-12), Diuron (PT 7, 10), Naphthalene (PT19); b) have been withdrawn from the review programme (Chlorpyrifos, Lindane); or c) have been identified for potential biocidal purposes but have not been notified (Endosulfan, Hexachlorocyclohexane, Pentachlorophenol, Simazine, Trichloromethane). The overlap with plant protection active substances is evident. These priority substances are included in monitoring programmes and Directive 2008/105/EC describes environmental quality standards for the 33 priority substances /substance groups.

According to Brack et al. (2007, 2009) numerous studies did not demonstrate a clear cause–effect relationship between environmental concentrations of priority pollutants and ecotoxicological effects or ecological status at many sites under investigation. Thus, the limited number of chemicals on the priority pollutant list may not be the sole or major driving force for poor ecological status at many sites. As chemical analysis of pre-selected sets of toxicants often does not explain the ecotoxic effects of complex environmental samples, the authors propose a combined biological and chemical-analytical approach for the identification of newly emerging toxicants (Brack et al., 2007, 2009).

Under REACH, the first candidate list of Substances of Very High Concern (SVHCs) was published in October 2008 with 18 substances identified as SVHCs fulfilling the criteria set out in Article 57 (carcinogenic, mutagenic, reprotoxic cat. 1 or 2, PBT or vPvB or similar concern as endocrine disruptors). Currently 38 substances are identified as SVHCs. 11 of these substances are currently prioritised for evaluation in the authorisation process. Among these prioritised substances are several which have been identified as existing biocidal active substances: Diarsenic Pentaoxide, Dibutyl-phthalate (DBP), sodium dichromate and bis(tributyltin)-oxide (TBTO). Boric acid, and disodium tetraborate, anhydrous are supported in the Review Programme of the BPD.

Endocrine effects were considered by a German study on sustainable and pre-cautionary risk assessment and risk management of chemicals. Among the endocrine disruptors that should be given high priority in risk assessment about 20 biocidal active substances have been identified, among them Lindane and several tributyltin compounds used as antifouling agents (Gies et al., 2001). None of these substances are supported anymore in the BPD Review Programme.

Within the EU funded project "Source Control Option for Reducing Emissions of Priority Pollutants" (ScorePP), comprehensive and appropriate source control strategies to reduce priority pollutant emissions to urban waterways were analysed. The project focuses on the 33 priority pollutants initially identified in the Water Framework Directive (Seriki et al. 2008).

To summarise: the existing lists of priority substances do not specifically consider biocides and monitoring of these substances alone does not seem to be appropriate for the identification of failures in sustainable use of biocides. Furthermore, biocides included in these lists have mostly been banned and their occurrence in the environment is due to historic use only.

Prioritisation of biocidal active substances for environmental monitoring:

An analysis of extensive monitoring data of water suppliers in Europe revealed that (with the exception of Triclosan) biocides are rarely included in monitoring programmes. Among the pesticides most often detected are herbicides, with some of these herbicides, such as Atrazin, having been banned in Europe, indicating the historic pollution of soil deposits[9]. For the Danube catchment area arsenic, copper, zinc, chromium and their compounds have been identified as priority substances specific for the Danube, and biocides may contribute to emissions of these metals. The herbicides Isoproturon and Chlorotoluron, which are also used as algaecides in several PTs, have been analysed in more detail. The results suggest that agriculture is a major source of emissions (IKSR, 2005).

The COWI-study set out assumptions regarding the most important biocidal active substances within each PT in terms of annual production volume in the EU, as described in table 3.

After exclusion of readily biodegradable active substances (e.g. benzoic acid and sodium benzoate), oxidising agents (e.g. chlorine and hydrogen peroxide) and fumigants (e.g. ethylene oxide and trimagnesium phosphide), this list might provide a first indication of candidate active substances to be monitored in environmental samples.

[9] According to Hanke et al. (2007) Atrazin is still used in Switzerland where is belongs to the 20 most important pesticides.

Table 3: Most important biocidal active substances within each PT in terms of t/a. Substances listed alphabetically, not ranked (COWI, 2009)

PT	Main Group 1: Disinfectants and general biocidal products	PT	Main Group 3: Pest control
1	Benzoic acid, pentapotassium bis(peroxymonosulphate)-bis(sulphate), sodium benzoate, sodium hypochlorite	14	Bromadiolone, chloralose, chlorophacinone, coumatetralyl
2	Chlorine, ethylene oxide, hydrogen peroxide, sodium hypochlorite, symclosene, troclosene sodium	15	Chloralose
3	Chloroxylenol, cyanamide, formic acid, glutaral, hydrogen peroxide, sodium hypochlorite	16	-
4	Chlorine dioxide, hydrogen peroxide, L-(+)-lactic acid, peracetic acid, sodium hypochlorite	17	-
5	Biphenyl-2-ol, chlorine, chlorine dioxide, potassium permanganate, sodium hypochlorite	18	Cyanamide, dichlorvos, phenothrin, piperonylbutoxide, propoxur, pyrethrin and pyrethroids
		19	Ethyl-N-acetyl-N-butyl-beta-alaninate, methyl neodecanamide, naphthalene
	Main Group 2: Preservatives		**Main Group 4: Other biocidal products**
6	1,2-benzisothiazolone, bronopol, (ethylenedioxy)dimethanol, guazatine triacetate, isothiazolone mixture, L-(+)-lactic acid	20	Chlorine dioxide
7	Carbendazim, dichlofluanid, diuron, tolylfluanid, triclosan	21	4,5-dichloro-2-octyl-2H-isothiazol-3-one, diuron, zineb
8	Boric acid, copper oxide, didecylpolyoxethyl ammonium borate, disodium tetraborate, guazatine triacetate	22	2-butanone peroxide, dodecylguanadine monohydrochloride, methylene dithiocyanate
9	(Benzothiazol-2-ylthio)methyl isocyanate, 2-chloroacetamide, chlorocresol, diphenoxarsin-10-yl oxide, disodium tetraborate, ziram	23	Trimagnesium phosphide
10	2-chloroacetamide, 2-phenoxyethanol, pine extract		
11	Chlorine, chlorine dioxide, hydrogen peroxide, silver zeolite A, sodium hypochorite, tetrakis(hydroxymethyl)-phosphonium sulphate		
12	Bronopol, 2,2-dibromo-2-cyanoacetamide, hydrogen peroxide, glutaral, peracetic acid, sodium dimethyldithio-carbamate, sodium hypochlorite		
13	Boric acid, disodium tetraborate, (hexahydro-1,3,5-triazine-1,3,5-triyl)triethanol, trimethyl-1,3,5-triazine-1,3,5-triethanol		

Table 3 does not consider the current status of the review programme. For example, the wood preservative guazatine triacetate has not been approved for Annex I inclusion and therefore it should not have been used as a biocidal active substance since June 2008. In Switzerland the following candidate biocidal substances with relevance for surface water have been pre-selected within the BIOMIK project, based on consumption and degradability data (Knechtenhofer et al., 2007; Bürgi et al., 2009, see table 4)[10]:

Table 4: Candidate biocides for surface water monitoring in Switzerland

Name	CAS
Boric acid	10043-35-3
Carbendazim	10605-21-7
Dichlofluanid	1085-98-9
Glutaral	111-30-8
Copper oxide	1317-38-0
Diethylamine *(was not identified as biocidal active substance !)*	109-89-7
N,N-diethyl-m-toluamide	134-62-3
Pyrithione zinc	13463-41-7
1,2-benzisothiazol-3(2H)-one	2634-33-5
2-octyl-2H-isothiazol-3-one	26530-20-1
N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine	28159-98-0
Diuron	330-54-1
Triclosan	3380-34-5
Formaldehyde	50-00-0
Bronopol	52-51-7
Permethrin	52645-53-1
3-iodo-2-propynyl butylcarbamate	55406-53-6
Diphenoxarsin-10-yl oxide	58-36-6
Propiconazole	60207-90-1
1,3-bis(hydroxymethyl)-5,5-dimethylimidazolidine-2,4-dione	6440-58-0
Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl, chlorides	68391-01-5
Terbutryn	886-50-0

In Switzerland, the total consumption of 277 different biocides has been estimated as being 7.500 t/a. More than 95% of this use is based on 30 active substances, of which seven are rapidly biodegradable (Bürgi et al., 2009).

The IKSR (Internationale Kommission zum Schutz des Rheins) publishes lists of chemical substances considered as being relevant for the Rhine River and several

[10] The criteria set by the group of experts for selecting these 22 substances as candidates for an extended assessment remain unclear as formaldehyde and glutaral should be biodegraded in WWTPs.

biocides supported in the Review Programme have been included in the list from 2007: Chlorocresol, Copper, Chlorotoluron, Dichlorvos, Diuron, Fenitrothion, Isoproturon, Monolinuron and Naphthalene (IKSR 2007, see also Annex III).

All these attempts to prioritise biocides as potential pollutants and to include some of them into monitoring programmes are based on expert knowledge rather than through the application of systematic methods. One option for improving the sustainable use of biocides could be to include typical biocidal actives which are emitted to the environment into respective monitoring lists. In order to prioritise potential biocidal pollutants for monitoring, emission data should be considered in conjunction with key properties of the substances, such as adsorption or biodegradation properties.

Götz et al. (2010) proposed a simple exposure based methodology for pre-selecting microcontaminants. This method is based on the annual consumption of the pollutants, physical–chemical properties and information about degradation and input dynamics. The method only requires the input of publicly available data on the chemicals' distribution behaviour between different environmental media, degradation data, and input dynamics. Ranking is based on a chemical's potential to occur in the water phase of surface waters. The three criteria used consist of (1) the chemical's distribution between media (water solubility, volatility or sorption), (2) the chemicals' biodegradation half-life in water, and (3) the input dynamics (continuous or repeated pulse input). The goal of this categorization methodology is to support the selection of compounds for water protection policy guidance and the identification of appropriate monitoring strategies. Table 5 shows the attribution of exposure categories to some biocides included in the study.

Table 5: Exposure categories of biocides from Götz et al. (2010)

	Exposure category	Water phase	Persistence	Input dynamics	Potential to occur in surface water	Monitoring data (av. conc. ng/L)
Carbendazim	III	≥ 10%	moderate	continuous	High	19
Diuron	IV	≥ 10%	moderate	complex	high	51
Terbutryn	IV	≥ 10%	moderate	complex	high	19
Irgarol	IV	≥ 10%	moderate	complex	high	5
Permethrin	V	≤ 10	not considered		moderate-low	not found

Most biocides attributed to isothiazolinones (e.g. octylisothiazolinone, benzisothiazolinone and chlormethylisothiazolinone) and quaternary ammonium compounds (e.g. benzyldimethyldodecylammonium-chloride and miristalkoniumchloride) have been attributed to exposure category III.

For biocidal applications with releases to municipal treatment plants this approach could be used to pre-select biocides to be included in monitoring programmes. However, data on total consumption of the active substances are required for this approach to become effective.

The need for improving the use of monitoring data in the exposure assessment of industrial chemicals has been challenged in an OECD workshop where it was recognized that the importance of monitoring data was proportional to the level of exposure assessment being performed (i.e., local, regional or continental). High priority was also given to improving accessibility to monitoring data. A number of recommendations regarding improvements to the design and performance of monitoring programmes were made, including calls for improved access to information on chemical emissions and for a dialogue between risk assessors and the monitoring community to be established (OECD 2000).

A strategy is being developed for the control of emissions of several pollutants detected in surface water of the river Rhine, including the bicoides Butylhydroxytoluene, Benzotriazole, Carbendazim, DEET, Mecoprop, and Triclosan (IKSR 2010).

Passive sampling

Passive sampling is a tool to monitor the presence and concentrations of micropollutants in the aquatic environment and has successfully been applied to the monitoring of biocides. The choice of the sampling material, the duration of integrative sampling, hydrophilic or hydrophobic properties of the micropollutants and the flow rate all have a significant influence on the results obtained (Vermeirssen et al. 2009).

3.3 Available data for each product type

As there is no systematic collection of data on the manufacture, consumption and occurrence of active substances (and their metabolites) in the environment, the following discussion sets out the data found in the literature research so far, arranged by PT. As well as quantitative data identified in the research, data found on relevant metabolites and degradation, usage in different applications (e.g. more than one PT or usage outside the scope of the BPD), and data on specific emission pathways is also considered.

PT 1: Human hygiene biocidal products

Triclosan and silver containing nanoparticles have been reported as biocidal active substances for hygienic purposes (Hund-Rinke et al., 2008). A Danish survey on the amounts of triclosan used as a preservative and antibacterial agent in cosmetics, cleaning materials, paint, textiles and plastic showed that in 2004 in total 1.8 t had been consumed, with cosmetics being by far the largest contributor to the amount of triclosan on the Danish market (99%). The largest amount of triclosan in cosmetics is found in products for dental hygiene, including tooth paste (Borling et al., 2006).

PT 2: Private area and public health area disinfectants and other biocidal products

The emission of disinfectants from hospitals into wastewater has been analysed by Gartiser et al. (2000). In summary, the average total consumption of active ingredients applied in hospitals for surface, instrument and skin/hand disinfection was found to be 27 g/(bed*day), with alcohols, which evaporate for the most part and therefore do not reach the sewer, representing the majority of emissions. Excluding alcohols, the consumption of active substances was 4.4 g/(bed*day), corresponding to a wastewater concentration of around 9 mg/l, with skin and hand disinfectants representing 10-15% of total consumption. in addition, the input of large kitchens and laundries to the consumption of biocides should not be ignored, as these uses contribute up to 99% of total loads of chlorine or peroxides, and up to 28% of total load of quaternary ammonium compounds (QACs). These data have been confirmed in a more wide ranging study including 27 German hospitals. Consumption data per bed and day and per nurse and day for particular categories of active ingredients corresponded quite well with the default values from the EU emission scenario documents (Tluczkiewicz et al. 2009).

Within a further German study on health risks from the daily use of biocide-containing products a market research was conducted and consumption estimates for washing and cleaning agents registered in Germany were analysed. The study revealed that total emissions of sodium hypochlorite, di- and tri-chloroisocyanuric acid and hydrogen peroxide from bleaching applications, are far greater than from their use for disinfection purposes. Also, the main emissions of isothiazolinones, benzoic acid, glutaraldehyde, 2-phenoxyethanol and triclosan are from preservative applications (see Annex 2). Typical important disinfectants are 2-propanol, alkyldimethylbenzyl ammonium chloride, gluataraldehyde, formaldehyde and hydrogen peroxide (Hahn et al., 2005).

Disinfectants/antiseptic agents have rarely been included in programmes monitoring hazardous substances in water. However, the following examples have been reported by Daughton et al. (1999, see table 6):

Table 6: Disinfectants/antiseptic identified in environmental samples in Germany

Active substance	PTs	CAS	Wastewater treatment plant monitorings
Biphenylol	1-4, 6, 7, 9, 10, 13	90-43-7	routinely found in both influents (up to 2.6 µg/L) and effluents (removal was extensive)
4-Chloro-3,5-xylenol (Chloroxylenol)	1-6 [1)]	88-04-0	occasionally found in both influents and effluents (< 0.1 µg/L)
Chlorophene	1-4, 6 [2)]	120-32-1	routinely found in both influents (up to 0.71 µg/L) and effluents
3,4,5,6-Tetrabromo-o-cresol	Not identified as existing active substance	576-55-6	found in both influents and effluents (<0.1 µg/l)
Triclosan	1-3, 7, 9, 11, 12	3380-34-5	0.05 – 0.15 µg/L in water

1) Not included in Annex I, COM Decision 2008/809/EC
2) Not included in Annex I for PT 1, 4, 6, COM Decision 2008/809/EC

Monitoring data from Austria show that QACs are effectively removed in municipal wastewater treatment plants. In the inflow DDAC-C10 and DDAC-C18, as well as BAC-C12 and BAC-C14, have been detected at the level of several µg/L. The total load of all QACs after treatment was considerably reduced and DDAC was rarely detected in the outflow of the WWTPs (Gans et al., 2005, see table 7).

Table 7: Monitoring of surface water and sediments by the Austrian Environmental Agency revealed the following concentrations (cited by Morf et al., 2007)

	Substance	CAS	Surface water µg/L	Sediment µg/kg
BAC-C12	Benzododecinium chloride (1)	139-07-1	0-1.9	3-3600
BAC-C14	Miristalkonium chloride (1)	139-08-2	0-0.5	0-1600
BAC-C16	Cetalkonium chloride (1)	122-18-9	0-0.1	1-350
BAC-C18	Benzyldimethyl(octadecyl)ammonium chloride (1)	122-19-0	0-0.1	0-290
DDAC-C10	Didecyldimethylammonium chloride	7173-51-5	0-1.5	0-510

(1) In the Review Programme of the Biocidal Product Directive these substances are covered by one entry: Quaternary ammonium compounds (benzylalkyldimethyl (alkyl from C8-C22, saturated and unsaturated, tallow alkyl, coco alkyl, and soya alkyl) chlorides, bromides, or hydroxides)/BKC.

From these data it is evident that, although low quantities of these QACs are detected in surface water, they are primarily adsorbed to sediments.

In a survey of 49 WWTPs in Germany, Biphenyl-2-ol (CAS 90-43-7, PT 1-4, 6, 7, 9, 10, 13) and Chlorophene (CAS 120-32-1, PT 1-4, 6) have been routinely found in both influents and effluents (up to 2.6 µg/L Biphenylol and up to 0.71 µg/L Chlorophene). The removal of chlorophene from the effluent was less extensive than for Biphenylol, with surface waters having concentrations similar to that of the effluents (Ternes et al., 1998).

The environmental impact of the increasing use of antibacterial silver used in medicinal products and products of everyday use has been assessed by Hund-Rinke et al. (2008). The preliminary risk assessment indicated that an environmental risk for the aquatic compartment and for sewage treatment plants can be considered as small, but cannot be totally excluded. For soil and sediment there is an indication of risk but current knowledge is limited on the concentration of silver ions in the environment, the influence of changing environmental conditions on silver and silver nanoparticles. Furthermore, washing machines containing silver electrodes are marketed which function as PT 2 biocides with silver released by electrolysis

(Samsung Electonics). General purpose and swimming water disinfectants may also contain silver in combination with sodium hydroxide (Sanosil).

PT 3: Veterinary hygiene biocidal products

Chemical disinfection of stables is routinely performed when animals are replaced. The main exposure route of these biocides is to liquid manure storage. The total amount of biocidal products used for this application in Germany was estimated as 860 t/a (about 60% for poultry farming and 40% for pig keeping). For cattle keeping, milking cleaners and disinfectants contribute to 22.000 t/a (Kaiser et al. 1998). The main disinfectants used are sodium hypochlorite, sodium dichloroisocyanuric acid (CAS 2782-57-2), sulphamidic acid (CAS 53429-14-6, only identified active substance), and several QACs (Didecyldimethylammonium chloride and benzalkonium chloride). In addition, about 250 t/a of Cyanamide (CAS 420-04-2, supported for PT 3 and 18) are used for liquid manure treatment to prevent the development of midge larvae. The emissions of disinfectants regarded as veterinary pharmaceuticals to liquid manure are also considered of major importance. Iodine-containing udder disinfectants (3.500 t/a) are also used, as well as copper sulphate, for prophylactic disinfection and protection of calves (1000 t/a) (Kaiser et al., 1998).

The German Environmental Agency funded a project to investigate the biodegradability of biocides in liquid manure (Kreuzig et al. 2010a, 2010b, see PT 18)

PT 4: Food and feed area disinfectants

A study of the German Environmental Agency on wastewater from bottle and tank cleaning processes provides a general overview of relevant processes and disinfectants applied. Wastewater pollution was assessed with bioassays (Pluta et al. 1997).

Currently a FIOSH project on human exposure to disinfectants applied to the food and feed areas is being planned (project number F 2034). The focus of this project will be on inhalation and dermal exposure. This project will also provide general data on the consumption of disinfectants.

PT 5: Drinking water disinfectants

Drinking water disinfection is based on oxidative biocides such as chlorine, sodium hypochlorite, calcium hypochlorite, chlorine dioxide, and ozone. In a German study on silver containing biocides, water treatment (including drinking water) has been identified as main source of silver emissions to WWTPs and the environment. This assumption is based on data from the Silver Institute which stated that in Europe 75% or 48,000 kg of biocidal use of silver in Europe is used for water treatment and ends up in WWTP. However, data might be overestimated, because legal requirements for drinking water treatment in Germany limit the concentration of silver in drinking water (Hund-Rinke et al., 2008).[11] A further biocidal use of silver is for the coating of terminal drinking water filters. This has been suggested as an appropriate method to protect immunocompromised patients from water-borne pathogens, such as Legionella (Vonberg et al., 2008).

PT: 6: In-can preservatives

A typical PT6 biocide which has often been analysed in wastewater and surface water is triclosan, a chlorinated biphenyl ether which is known to be highly toxic to aquatic organisms (Orvos et al. 2002; Singer et al., 2002; Thompson et al., 2005). The reason for the good data on triclosan emissions is that this substance is often analysed together with pharmaceuticals, because it is also used in medicinal personal care products (Paxeus, 2004; Thomas, 2004; Quintana, 2004; Bendz et al., 2005).

An analysis of plant protection products identified in ground and drinking water by drinking water suppliers indicated that the herbicides Diuron, Isoproturon and Chlorotoluron are among the 20 plant protection products most often detected in water samples (Sturm et al., 2007). In addition to their application as herbicides for plant protection purposes, these substances are also supported as biocides for PT 6 and 7 (and to a lesser extent for PT 9-13). However, the contribution of biocides to the total emissions of these contaminants remains unclear.

PT 7: Film preservatives

Among the biocides used in paints and plasters, Carbendazim, Diuron and Mecoprop[12] have often been detected in the different environmental compartments.

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[11] According to another study silver is mainly used for mobile drinking water purification and its permanent use for drinking water disinfection is restricted (Gartiser et al. 2005).

[12] The herbicide Mecoprop (CAS 93-65-2) has not been identified as a biocidal active substance and should not be used for that purpose.

All these substances are active ingredients in material protection products. Mecoprop used in bitumen sheets for roof waterproofing was investigated more specifically. Initial laboratory tests found leaching rates differing by a factor of 100 between different products (Burkhardt et al., 2007).

The leaching of four biocides (Diuron, Terbutryn, Cybutryn, Carbendazim) used in resin based facade coatings has been investigated by Burkhardt et al. (2009). Leaching from the facade was tested under UV-irradiation over 28 days using 80 irrigation intervals. This study found high initial concentrations followed by an exponential decrease. Rising temperature was found to increase the concentration of biocides in the runoff and the total losses were between 7% and 29% depending on the biocide. More than half of the losses occured within the first 15 min of runoff from a 60 min irrigation cycle. In the first litre of facade runoff 7 mg/L Diuron and 0.7 mg/L Carbendazim were detected. The authors further concluded that the modelling result for Cybutryn (28159-98-0, PT 7, 9, 10, 21) highlighted the high environmental risk to small surface waters from this substance. Diuron and Carbendazim are also used as pesticides and preservatives for other materials hence all pathways have to be evaluated in order to identify relevant sources and to protect soil and water receptors from these substances more efficiently (Burkhardt et al., 2009).

Terbutryn, a methylthiotriazines algicide and herbicide , is still supported as a biocidal active substance for PT 7, 9 and 10, while its approval as a plant protection agent in Germany was recalled in 1997 and in most other European countries in 2004. Despite its removal as a plant protection agent, monitoring programmes performed in 2005/2006 by the German Environmental Agency revealed that Terbutryn is detectable in most surface water samples in concentrations of up to 48 ng/L ((Kahle et al., 2009). In Bavaria in 2006 Terbutryn was detected in river water at maximum concentrations of 20 ng/L (Danube), 110 ng/L (Main) and 140 ng/L (Regnitz) (LfU Bayern, 2007, cited in Kahle et al. (2009). In the Elbe, 2.4 ng/L has been detected (Gerwinski, 2002).

The leaching rates of biocides from roof paints have been determined in laboratory experiments (application of paints to glass plates, drying for 24 h, dipping in synthetic rain water, exchanging of leaching solution every 24-72 h over 40 days). The release rates of Carbendazim and Terbutryn respectively were 12 mg/m^2 and 58 mg/m^2.In roof drain water concentrations of 9 mg/L and 1.5 mg/L of these biocides have been detected at low rain intensity (0.3 mm/h). This leaching study found that the concentrations of selected biocides may reach significant levels, especially after low intensity rainfall. Concentrations dropped with increasing time and rain intensity. No kinetics could be derived for methylisothiazoline-3-one and octyl-isothiazoline-3-ones as concentrations measured were below the detection limit which may have been caused by rapid biotic degradation and/or photodegradation (LUA NRW, 2005, Jungnickel et al., 2008).

PT 8: Wood preservatives

In Regulation 2032/2003 about 80 active substances were listed for PT 8, of which 41 active substances were included in the EU review programme for evaluation and possible inclusion in Annex I, IA or IB to Directive 98/8/EC[13].

In Germany, the total consumption of wood preservatives has been estimated to be approximately 29.000 – 31.000 t/a (Langer and Forst, 2001; OECD, 2003, cited in Gartiser et al., 2006). The consumption of wood preservatives in Germany can be divided into the following user sectors (see table 8):

Table 8: Consumption of Wood Preservatives in Germany (formulated products)

Application process	Amount [t/a]	[%]
Pressure treatment (water and solvent based, without tar oil)	2.000-2.200	7.0
Treatment in dipping/immersion plants	4.700-4.900	16.1
Tar oil; pressure and hot/cold dipping	5.000-6.000	18.3
Industrial/professional preventive treatment (injection, brushing) undercoating, varnishing, impregnation	12.400-12.600	41.8
Professional market undercoating, varnishing, painting	1.750	5.9
Do-it-yourself market undercoating, varnishing, painting	1.750	5,9
Professional curative treatment (injection, brushing)	1.750	5,0
SUM	29.000-31.000	100

Source: OECD Emission Scenario Document No. 2, Part I; ➔ http://www.oecd.org/dataoecd/60/11/2502747.pdf

13 Up to March 2009, 10 active substances of PT 8 have been included in Annex I or IA to Directive 98/8/EC: Clothianidin, Dichlofluanid, Etofenprox, IPBC, K-HDO, Propiconazole, Sulfuryl fluoride, Tebuconazole and Thiamethoxam

The above table shows that in Germany about 53% of wood preservatives are for professional applications, about 43% for industrial applications and about 6% for do-it-yourself applications. Table 8 also shows that about 95% of wood preservatives are applied in preventive treatment and only about 5% in curative treatment.

For Denmark, the total consumption of wood preservatives was quoted to range from 393 – 474 t/a (Lassen et al., 2001). COWI (2009) presents similar figures for the Danish consumption of wood preservatives: 377-453 t/a for vacuum and pressure applications and 16-21 t/a for for surface treatment, respectively.

Morf et al. (2007) present consumption data for wood preservatives in Switzerland where consumption is estimated to be approximately 1.098 t/a, corresponding to ca. 14.8% of total biocide consumption.

According to COWI (2009) the total annual tonnage for PT 8 in the EU amounts to 11.233 t/a, corresponding to 2.8% of the total tonnage for all PTs. This figure comprises the annual production/import volume for the active substances used in PT 8 in Europe and is based on data provided to the European Chemicals Bureau by companies as part of the notification procedure. (The lower figure compared to the consumption volume given for Germany in the OECD ESD of table 8 is due to COWI data being based on active substances tonnages while the OECD ESD estimates are based on formulated products.)

COWI (2009) further states that the use of wood preservatives is more important in cool and humid northern Europe than in the south. The most important active substances used in PT 8 in terms of production tonnage (1998-2001) are boric acid, cooper oxide, didecylpoly-oxethyl ammonium borate, disodium tetraborate and guazatine triacetate.

Exposure of the environment to PT 8 biocidal products may take place both in the application phase and in the service-life phase. This is particularly true for preservatives that are used both by professional and non-professional users for the surface treatment of wood which may be emitted to all environmental compartments (air, soil, water) and to WWTPs. In contrast, vacuum and pressure preservatives are mainly used by professional users in specialised plants so that exposure is limited to the air and WWTPs (COWI, 2009).

One possible emission pathway of biocides (including wood preservatives) into surface water may be rainwater discharges (in case of separate sewer systems) or storm water overflows. In both cases rainwater may be contaminated with biocidal active substances that are used in outdoor applications like fence poles, roofs or facades. However, knowledge about the quantities of biocide used for outdoor applications and leaching rates of the biocidal active substances is scarce, especially for wood preservatives.

Leaching rates for wood preservatives have been determined by Schoknecht et al. (2002, 2004) both in laboratory and outdoor experiments. Wooden poles treated with Propiconazol were exposed to rainfall and cumulated losses of Propiconazol were found to range between 100 mg/m² and 150 mg/m² within 200 days with rainfall of between 350 L/m² and 400 L/m². This loss corresponds to daily emission rates of 0.4 mg/m² for short poles with a smooth surface and of 0.7 mg/m² for longer poles with a rough surface. In the leaching tests a Propiconazol loss of 0.1 to 6.5 mg/m² per litre of rainwater was observed.

Leaching of wood preservatives may be particularly prevalent in wood impregnation plants which store treated wood in open storage areas, exposed to rainwater.

Copper containing preservatives have a market share of about 70% in pressure impregnation of wood, and consumption of between 70 t/a and 140 t/a copper containing wood preservatives has been calculated for Germany, with 3 t/a to 8 t/a being released through leaching, primarily to soil (Hillenbrand et al., 2005).

The leaching rate for wood preservatives depends mainly on the time required for the fixing process where the wood preservatives react with various constituents within the wood. During that period the risk of leaching by precipitation has to be minimised to ensure the efficacy of the preservation as well as to prevent emissions into the environment. Therefore, the German Umweltbundesamt funded a research project to determine the minimum fixing time for wood preservatives. This study found that the time necessary to reach a fixation level of 95% was typically between 2 and 14 days and depended on temperature and the active substance concerned. High air humidity increased the fixation time to upto 58 days (Schoknecht et al., 2003).

Direct emissions of wood preservatives to soil may also occur during the manual treatment (brushing) of fence poles. The fraction of product lost to the soil during application was determined to range from <.0.01% to 6% for Propiconazol and from 0.03% to 0.6% for Tolylfluanid. Here, the determining factors were wind speed, brushing speed and quantity of wood preservative applied per stroke of the brush (Uhlig et al., 2007; cited in Kahle et al. (2009).

Once the wood preservatives have dripped onto the soil they may be washed into surface water via run-off or they may leach further into the soil profile and ultimately enter the groundwater.

In surface water, a range of distribution processes between the water phase and the sediment take place the nature of which depend upon the physico-chemical properties of the active substances. For example, the wood preservative Permethrin tends to adsorb to sediments.

The active substances Propiconazol and Tebuconazol also used as wood preservatives have been detected in the effluent of WWTPs in Switzerland (Kahle et al., 2008, see PT 10). Propiconazol has also been included in groundwater monitoring programmes in Germany. In some groundwater samples Propiconazol was detected in concentrations upto <0.1 µg/L (and in 2 samples upto 0.1 µg/L and 1 µg/L, respectively). It was, however, not possible to allocate these values to specific emissions sources (Kahle et al., 2009).

Further monitoring data for wood preservatives were collected for the BIOMIK Project (Morf et al., 2007). In Canada, the QAC DDAC-C10 was detected in the Fraser River and downstream from four sawmills where the compound was used as wood preservative. DDAC-C10 concentrations in the sediment ranged from 0.52 mg/g to 1.26 mg/g dry weight with corresponding concentrations in the surface water of 446 µg/L close to the emission sources and <10 µg/L (LOQ) at a distance of 10 m from the emission source, respectively.

The insecticide Chlothianidin (CAS 210880-92-5), which has been included in Annex I of the BPD for PT 8 and is also supported for PT 3 and 18, was identified as the cause of a bee mortality incident which occurred in parts of South-West Germany in

April and May 2008 after maize seeds had been treated with Clothianidin (press release www.bvl.bund.de).

PT 9: Fibre, leather, rubber and polymerised materials preservatives

Some monitoring data are available for active substances used for PT 7, 10 or other PTs as well as being used for PT 9 purposes. However, no specific environmental emission data for PT 9 compounds have been found.

PT 10: Masonry preservatives

The occurrence and fate data for nine agricultural azole fungicides, some of them also used as biocides were studied for wastewater treatment plants (WWTPs) and lakes in Switzerland. The biocides Propiconazole (CAS 60207-90-1, PT 1, 2, 4, 7-10,12, 13, 20) and Tebuconazole (CAS 107534-96-3, PT 7-10) were consistently found in WWTP influents in concentrations of 1−30 ng/L. Loads determined in untreated and treated wastewater indicated that Propiconazole and Tebuconazole were largely unaffected by wastewater treatment. Incubation studies with activated sludge showed slow degradation and some sorption was observed for Tebuconazole and Propiconazole (degradation half-lives, 2−3 d). In lakes, Propiconazole and Tebuconazole were detected at low, nanogram-per-litre, levels. Per capita loads of Propiconazole and Tebuconazole in lakes suggested additional inputs; for example, from farm use or from urban rainwater runoff (Kahle et al., 2008). Furthermore, groundwater monitoring covering the federal states occasionally detected Propiconazol below 0.1 µg/L. The concentration of two samples was between 0.1 and 1 µg/L but the source of the contamination could not be identified (UBA-Grundwasser-Datenbank; Kahle et al., 2009).

Schoknecht et al. (2009) analysed the leaching behaviour of biocides used in facade coatings. These materials are increasingly used for textured coatings (renders) and paints for exterior façades where biocides are added to avoid the growth of fungi and algae on the surfaces of buildings, especially where effective thermal insulation prevents drying of the surface. The concentration of the active ingredients in the paints was around 1500 mg/kg and that in the render around 750 mg/kg.

In short-term immersion tests (Lab-ST) specimens with a coated surface area of 82.5 cm^2 were immersed in 200 mL of de-ionized water for 1 h. In the permanent immersion tests (Lab-PI) this procedure was prolonged for up to 29 days. In the irrigation experiments (Lab-IR) a coated surface area of 700 cm^2 was arranged on a 60° angled test assembly and irrigated with deionized water 10 times over 10 days (2.5 L/m^2 within 2 min of irrigation per day). Table 9 presents the main experimental results.

Table 9: Maximum concentration in the eluate and maximum emission rates of biocides from façade coatings

	Lab-ST		Lab-PI		Lab-IR	
	eluate mg/L	emission $mg/(m^2*d)$	eluate mg/L	emission $mg/(m^2*d)$	eluate mg/L	emission $mg/(m^2*d)$
1,2-benzoisothiazolin-3-one (BIT)	13.2	625	50.1	4651	24.5	58
2-n-octyl-4-isothiazolin-3-one (OIT)	38.	178	10.2	919	5.9	12
3-iodopropynylbutylcarbamate (IPBC)	1.2	57	4.4	244	2.3	6
Isoproturon	3.4	173	12.2	965	3.8	10
Diuron	2.3	111	6.7	570	3.3	8
Terbutryn	0.9	42	2.7	189	1.2	3
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT)	0.2	8	0.5	26	0.3	0.8
Carbendazim	0.3	14	3.8	149	0.4	1
Irgarol	0.8	40	2.3	196	1.3	3

Lab-ST: short-term immersion tests, Lab-PI: permanent immersion test, Lab-IR: irrigation experiments

The active ingredients that were added to the renders and paints were all detectable in the eluates of the different leaching tests. Emissions mainly occur at the beginning of leaching periods.

PT 11: Preservatives for liquid-cooling and processing systems

In a German study typical biocide concentrations and emission have been estimated for cooling water based on data on the consumption of biocides for 180 plants. Principal loads were found to come from open recirculation cooling systems, even though only <10% of the plants using once-through cooling water used conditioning chemicals at all. Extrapolation of these data to the consumption data for Germany as a whole produced estimates of total loads of about 4.000 t/a oxidative and 125 t/a non-oxidative biocides (Gartiser et al., 2002, see Annex 4).

PT 12: Slimicides

Slimicides are used to protect industrial processes such as paper manufacturing or oil and gas production against fouling and in both cases application is limited to professional users. There is considerable overlap between the use of both oxidative and non-oxidative biocides for cooling water treatment (PT 12). Slimicides used for paper manufacturing are released to the wastewater which is biologically treated either on-site or in municipal treatment plants. Available data suggest that environmental impacts are mainly considered in respect of the optimization of processes and impacts on the WWTPs concerned (http://www.ptspaper.de).

PT 13: Metalworking-fluid preservatives

The fungicide Imazalil (CAS 35554-44-0), which is supported for PT 2-4, 13 and 20, has been detected in the outflow from some wastewater treatment plants in concentrations of up to 10 ng/L (Kahle et al., 2008).

PT 14: Rodenticides

Many anticoagulant rodenticides, such as Difenacoum, Difethialone, or Flocoumafen, are persistent, liable to bioaccumulation and toxic (PBT criteria), and therefore subject to a comparative risk assessment before their inclusion in this Annex is renewed. The main concern regarding rodenticides is primary and secondary poisoning of wildlife or other non-target organisms (household animals). No data are available on the occurrence of anticoagulants in environmental samples; however, several studies describe incidents of wildlife poisoning. For example, in a British study Difenacoum was detected in 20% of raptors (tawny owls) (Walker et al., 2008).

PT 15: Avicides

No biocidal products of this product type may be authorised for use in Germany (German Chemicals Act (ChemG)), as well as in several other Member States, such as Austria and Switzerland. However, avicides may be authorised for use in other Member States, such as Spain and the UK. Currently, only two active substances (Chloralose, CAS 5879-93-3 and carbon dioxide) are supported for use as an avicide (and as well for PT 14 and 23).

PT 16: Molluscicides

According to the Borderline-Documents of the Commission regarding biocides and plant protection products this PT concerns products used against snails to prevent human and animal disease transmission and products used against snails that clog water pipes, as opposed to products used against snails that cause harm to plants.

However, in a German study on human exposure with PT 16 biocides it was shown that occupational exposure to these biocidal products is practically non-existent, and that overlaps exist between PT 16 biocides and cooling water biocides (PT 11) (Schneider et al., 2008). Consequently, no active substance at all has been supported for this product type.

PT 17: Piscicides

No biocidal products of this product type can be authorised in Germany or in other Member State (see PT 15).

PT 18: Insecticides, acaricides and products to control other arthropods

The main emission sources of biocidal insecticides are animal housing and applications in and around buildings. The OECD has developed two emission scenario documents: a) Insecticides for Stables and Manure Storage Systems and b) Insecticides, Acaricides and Products to Control Other Arthropods for Household and Professional Uses.[14]

Agricultural insecticides may be used for both the application in animal housings and in manure storage systems (larvicides). Land application of manure to soil is considered the main emission route while some insecticide may also be emitted to sewers and WWTPs. Non-agriculture insecticides are generally used in or around buildings where the presence of insect pests is unwanted. Insecticides are applied in private houses but also in public buildings, such as hospitals, and professional buildings, such as restaurants.

For indoor application to surfaces, insecticides generally do not directly reach environmental compartments. However, surface cleaning will lead to releases either to wastewater or to general waste. Therefore, WWTPs are considered as one of the main receiving compartments.

With regards to outdoor application, consideration has been given to spraying, powder application and bait stations. The fate of the substance released to the environment depends upon where the treatment is undertaken, i.e. either in the countryside or urban environments. In urban environments rain water will wash

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[14] http://www.olis.oecd.org/olis/2006doc.nsf/LinkTo/NT00000E62/$FILE/JT00197426.PDF
http://www.oecd.org/dataoecd/21/9/41030103.pdf

insecticides into the rain water/sewer system. For separate systems (rain water), it can be considered that no removal takes place at this point source. For mixed waste/rain water systems WWTPs will be the environmental compartment to be considered, followed by surface water or agricultural soil (from sludge application).

It has been suggested that veterinary drugs and biocides may be transformed in liquid manure reducing the total released to agriculture soils from manure application and storage (Montforts et al. (2004). A German research project developed a technical protocol for testing the behaviour of biocides in manure using standards with 10 % dry solids for bovine manure and 5 % dry solids for pig manure. These reference-manure samples were used for the degradability testing of the ^{14}C-labeled biocides Imazalil and Cyanamide. After a storage time of 177 days in the dark at 20°C no significant decrease of Imazalil concentration was observed. However, 77% - 90 % of the radioactivity initially applied remained in the extractable residues . In contrast, Cyanamid was significantly mineralised (16%) or bound to the dry solids and after 100 days the extractable residues accounted for 30% - 51% of the initial radioactivity (Kreuzig et al. 2010a, 2010b).

Monitoring data for pesticides from different water suppliers confirm that insecticides are rarely detected in surface water. (Herbicides are most often detected in concentrations above the drinking water limit value for pesticide residues of 0.1 µg/L).

WWTPs have been identified as important sources of pesticides emitted to the environment. However, these emissions cannot be attributed to biocides alone because malpractice during the application of plant protection products, such as losses during mixing and loading or the cleaning of equipment after treatment, is a major contributor to these emissions. The insecticides Diazinon and Primicarb used in households and gardens have been identified as a possible significant contributor to overall emissions to sewage (Balsiger, 2004).

In a study for the German FIOSH, mosquito control in the Upper-Rhine area via large-scale helicopter based application of *Bacillus thuringiensis* toxins has been analysed with a principle focus on human exposure. About 800 ha per day are treated with 8 t of ice granulate containing 80 kg active substance. Assuming 60 working days per year, the total amount of active substance applied to the environment comes to 10.8 t/a (Schneider et al., 2008). Another example for aerial spraying on a large scale from helicopters is the control of oak procession moths (*Thaumetopoea processionea*) whose fine hairs can cause allergic reactions to humans. The active substance used is generally Diflubenzuron (CAS 35367-38-5), at a dosage rate of 16 g active substance per hectare (=10^4 m^2). *Bacillus thuringiensis* toxins are used near bodies of water while Diflubenzuron must not be used within 100 m of such environments (Anonymous, 2008).

PT 19: Repellents and attractants

DEET (N,N-diethyl-m-toluamide, CAS 134-62-3, supported for PT 19 and 22) is one of the most important repellents against midges and has been detected in surface water all over the world. In the inflow and outflow of a WWTP in Hamburg concentrations of 210 ng/L and 130 ng/L, respectively, have been detected, indicating that DEET is not effectively removed during wastewater treatment (Weigel et al., 2004).

PT 20: Preservatives for food or feedstocks

The fungicide Imazalil is an example of a biocide used for PT 20 and other PTs (see PT13).

PT 21: Antifouling products

Antifouling products are used to treat vessels, other structures used in water, and aquaculture equipment, however the latter is not relevant to overall emissions. Globally about 95% of antifouling products are used for vessels (van de Plassche, 2004). In 2002 CEPE estimated the consumption of of marine paints and lacquers in the EU to be 9.540 t/a (www.cepe.org), but this volume covers all such products and not just antifouling products.

Organotins are the most widely used organometallic compounds with a worldwide production volume estimated at 50,000 tons. About 70% of the total amount is used as to produce PVC stabilizers, 23% is in agrochemicals and the rest is used in biocides for a wide range of applications (e.g. antifouling paints, wood and stone treatment, textile preservation, dispersion paints, industrial water systems), and as catalysts and reactants in chemical industry. In general the disubstituted organotins are used as PVC stabilizers and catalysts, and the trisubstituted organotins as biocides. Organotin compounds are released into the environment via several pathways, the most important of which are from agrochemicals, and antifouling paints, as well as from leaching from PVC (Baggenstoss, 2004).

A study of the Austrian Federal Environmental Agency revealed that the main sources of organotin compounds in the inland aquatic environment are antifouling coatings, plant protection products, wood preservatives, plastic stabilizers, textile impregnation, and disinfectants. The highest values were detected in sediments from surface water and sewage sludge. In surface water samples only some organotin compounds were occasionally detected (exception: monobuthyltin, a degradation product of tributyltin and stabilizer/catalyser of plastic which was detected at concentrations of up to 14 ng/L) (Sattelberger et al., 2002).

The International Convention on the Control of Harmful Antifouling Systems on Ships developed by the International Maritime Organisation (IMO) entered into force on 17 September 2008. This convention prohibits the use of harmful organotins in antifouling paints used on ships and will establish a mechanism to prevent the potential future use of other harmful substances in anti-fouling systems. The application of antifouling systems containing Tributyltin is globally banned for all ships.

As there is a multiplicity of measured data on organotin compounds in the environment available trends are difficult to establish. Therefore, concentrations detected in specific compartments often can give only a rough picture of overall contamination. For example, a distinction can be made between the normal concentrations is sediments and concentrations at “hot spots” e. g. in harbours and industrial sites. Concentrations in suspended matter and sediments often correlate to the proportion of municipal wastewater in the respective water bodies. Concentrations in the free water bodies is always significantly lower than in corresponding sediments because of the high affinity of organotins to sediments (Klingmüller et al., 2003).

A study of the working group on pollution control of the river Elbe gathered analytical data for organotin compounds in sediments from the Elbe. Here, up to 300 µg/kg Tributyltin (calculated as tin) has been detected which could explain the recorded environmental effects from monitoring data (Arge Elbe, 2001).

With regards to the marine environment, OSPAR (2006) estimated the total losses of substances from antifouling coatings to the Greater North Sea in 2002 (before the ban of organotin containing antifouling coatings) to be 300 t/a (copper), 1800 t/a (zinc), 130 t/a (tributyltin) and 5 t/a (other biocides from antifouling coatings).

As a German bulletin concerning the use of antifouling paints states, the most used substance is copper, as metal powder and in different copper compounds. However, in many cases other organic substances like Triazine (e.g. Irgarol 1051), Zinc-compounds (e.g. Zinc-Pyrithion, Zinc-naphthenat), Methylurea compounds (e.g. Diuron), Dithiocarbamate (e.g. Zineb, Maneb) are also added to the antifouling product to enhance the coatings efficacy (“booster biocides”) (Bayerisches Landesamt für Wasserwirtschaft, 2005; Readman et.al., 2002).

Currently, the 10 antifouling products included in Annex I for PT 21 are being evaluated, among them Tolylfluanid and Irgarol. Tolylfluanid, which is also being evaluated for its use under PT 7, 8 and 10, is degraded during drinking water ozonisation to N, N-Dimethylsulfamide (DMS), which is a precursor of the carcinogen N-Nitrosodimethylamine (NDMA). In Germany DMS has been detected in surface water (50 ng/L to 100 ng/L) and ground water (100 ng/L to 1000 ng/L) (Schmidt et al., 2008). The field use of Tolylfluanid containing PPPs is rising and since the 1980`s Irgarol (Cybutryne), (also PT 7, 9 and 10) has been used as a TBT substitute in vessel paint.

Extensive studies for the German UBA have shown that the negative environmental effect concentration of the active substance Cybutryne (Irgarol) found in mesocosm tests correlates to the real concentration measured in the environment (Kahle et al. 2009).

The usage of the new antifouling booster biocides Zinc pyrithione (ZnPT) and Copper pyrithione (CuPT) is increasing rapidly while problems continue with regards to the analysis of these substances (Raedman et al., 2002). These substances have been found to have very toxic effects on aquatic organisms, especially algae. When exposed to light in the water column they rapidly degrade to six main photodegradation products, the toxic effects of which are still under assessment (Onduka et al, 2007).

Zinc pyrithione (ZnPT) was examined by Grunnet and Dahllöft (2005), with regard to its fate in the marine environment (e.g. leaching from antifouling paints and the trans-chelation of ZnPT2 into CuPT2). This study produced a summary of how naturally occurring ligands and metals in seawater influence the stability of ZnPT2. The presence of free Cu^{2+}, which is present naturally in seawater, or as released from copper-containing paints, results in the partial trans-chelation of ZnPT2 into CuPT2. The complete trans-chelation of ZnPT2 into CuPT2 was observed when Cu^{2+} was present at an equimolar concentration in the absence of other “interfering” ligands When the leachate from antifouling paints containing both ZnPT2 and Cu_2O was analysed, CuPT2 was found, but no trace of ZnPT2. Photodegradation was low in natural waters and absent from 1 m or more below the surface. The results show that ZnPT2 has a low persistence in seawater when leached from antifouling paints. However, the more stable and toxic trans-chelation product CuPT2 has the potential to accumulate in the sediments and, therefore, should be included in both chemical analysis and risk assessment of ZnPT2 (Grunnet et al., 2005).

The environmental impacts of alternatives to the application of antifoulings have also been assessed. These products consist of a silicon resin matrix and may contain unbound silicon oils (1-10%). If these silicon oils leach out, they can have impacts on the marine environment: PDMS are generally persistent, they adsorb to suspended particulate matter and may sediment with them. Therefore, marine sediments are their ultimate sink. Furthermore, at high concentrations, an oil film may build up on sediments, and the infiltration of pores may inhibit pore water exchange, resulting in anoxic conditions with indirect effects on benthic communities. Non-eroding silicon-based coatings, which reduce fouling of ship hulls, do not bioaccumulate in marine organisms and have low direct toxicity for aquatic and benthic organisms. Metabolites, though formed at very low rates, are bioavailable, subject to long-range transport, bioaccumulate because of their small molecular size, transfer along trophic chains and have significant toxic potential. Therefore, such metabolites must be considered in silicon oil assessments. However, up to now considerable information gaps exist, preventing a sound assessment of potential impacts (Nendza, 2007).

For active substances used in antifouling products emissions from the treated surfaces (for example, ships’ hulls or fish nets used in aquaculture) are critical to any robust exposure assessment. With regards to exposure assessment the review programme uses the OECD guidance entitled, “Emission Scenario Document on Antifouling Products” (OECD, 2005). A critical input parameter for estimating emissions is the leaching rate, which is part of the additional data set for this product type. Under the progress of the review programme the determination of the leaching rate was discussed several times in the Biocides Technical Meeting (TM). One crucial factor for estimating emissions in a statistical model is the total dry film thickness. It is essential that Member States always determine the number of coats required for each antifouling product plus the predicted dry film thickness of each coat in order to ensure that the total dry film thickness is used in the CEPE calculation method (for example, if a product must be applied as 3 coats of 150 μm per coat, then the total dry film thickness used in the CEPE model must be 450 μm). However, considering that most coating types work by erosion/polishing of the existing paint layer to expose new layers containing active substance, the UK believes that the assumption used in the CEPE model, that only 70% of active substance in the overall coating will be released over the lifetime of that coating could result in a considerable underestimate of overall emissions, as products would still be released until the very last layer was exposed. The potential release of biocide should be considered to be nearer to 100%, over the lifetime of the paint. However, from published literature it is evident that erosion on some parts of the hull occurs more slowly than other areas, and so not all of the active substance would be released at the end of the service life of the paint. Therefore, whilst the UK does not agree with the assumed loss of 70% of active substance, the UK also considers 100% loss to be unrealistic. Therefore, it could be suggested that the determination of leaching rate should be based upon an anticipated loss of 90% of active substance into the environment as a default value until data become available to support the use of a more definitive value (Andres et al., 2006).

Currently some Member States have specific national Regulations on antifouling products (Limnomar, 2004). For example, in Denmark antifouling paints containing Diuron or Irgarol are banned for vessels with lengths < 24 (www.mst.dk). Similar national provisions apply in Sweden (www.kemi.se), the Netherlands (www-ctb-wageningen.nl), and the UK (www.hse.gov.uk).

PT 22: Embalming and taxidermist fluids

About 25 active substances form different chemical classes are included in the Review Programme for this PT (QAC, aldehydes, DEET, anorganics etc.). However, no specific environmental data relating to this product type have been found.

PT 23: Control of other vertebrates

No biocidal products of this product type can be authorised in Germany or in any other Member State (see PT 15).

4 Further aspects of sustainable use

4.1 Human exposure

Compared to the situation for environmental concentrations, far more information is available on human exposure to biocides. Such information may be an indirect indicator of use patterns which result in emissions to the environment. In a German Environmental Survey of children, several biocides were analysed in the 63 µm dust fraction. Despite the fact that Pentachlorophenol (PCP), DDT and Lindane have been banned, they are still present in household dust samples. Chlorpyrifos and Methoxychlor were detected in 32% and 24% of samples, respectively; while Polychloro-2(chlormethylsulfonamid)-diphenylether and derivatives (PCSD/PCAD) were detected in 15% of household dust samples. Hexachlorobenzol and Propoxur were detectable in only 2% and 6% of samples respectively (Müssig-Zufika et al., 2008). In the same survey of children, PCP and other chlorophenols, as well as pyrethroid metabolites, were detected in urine samples where the PCP was mainly attributed to the historic use of this substance as a wood, textile and leather preservative (Becker et al., 2008).

A study on human exposure to pyrethroids used as insecticides for pest control and wool carpet preservation (private and occupational settings), concluded that, provided that best practices are applied, no evidence of risks to humans could be identified from biological monitoring (BMBF, IVA 2001). In another study, emissions of formaldehyde or formaldehyde releasing compounds as well as Isothiazolinones (2-Methyl-4-isothiazolin-3-one (MIT) and 5-Chlor-2-methyl-4-isothiazolinone (CIT)) from paints to air were investigated. One day after application the CIT concentration was determined to be between 15 and 85 µg/m^3, with a corresponding MIT concentration of below 5 µg/m^3. Both concentrations were observed to decline within seven days to below their respective detection limits (Horn et al., 2002).

In a US study, the persistence of organic wastewater contaminants in a conventional drinking-water treatment plant were assessed (Stackelberg et al., 2004). This study determined the occurrence and fate of 106 organic wastewater-related contaminants (including plant protection and biocidal active substances) during drinking water treatment. The study revealed that, among the active substances supported in the

Review programme, only DEET (PT 19) and Triclosan have been detected in stream and raw water samples, while Diazinon (CAS 333-41-5, PT 18), Dichlorvos (CAS 62-73-7, PT 18), and Limonene ((R)-p-mentha-1,8-diene, CAS 5989-27-5, PT 12) have not been found. In a further study, the occurrence and biodegradability of several antiseptics used in personal care products were analysed (Yu, 2006).However, the scope of this literature review is limited to European data.

4.2 Impacts on biodiversity, non-target organisms, and resistance

The BPD aims to ensure a high level of protection for humans, animals and the environment. It has however been suggested that the BPD should also include further objectives and prerequisites, such as biodiversity or (ground) water protection against metabolites, particularly with respect to the approval of active substances. While the impact of biocidal products on non-target organisms is assessed during the evaluation process, up to now biodiversity is not mentioned as a protection goal of the BPD. However, active plant protection substances whose use would result in unacceptable environmental effects, e.g. negative impacts on biodiversity, would not be allowed under the draft regulation to replace Directive 91/414EEC..

Directive 92/43/EEC on the conservation of natural habitats and of wild fauna and flora includes provisions that require the maintenance or restoration of the natural habitats and populations of species of wild fauna and flora, including terrestrial or aquatic areas that contribute to ensuring biodiversity. In the context of Directive 92/43/EEC the use of biocides in general or of specific modes of application (such as spraying) in sensitive areas should be avoided.

Evidence of exposure of wildlife to biocides is scarce (with the exception of antifouling agents). One example is the detection of anticoagulant rodenticides such as Difenacoum in 20% of raptors (tawny owls) in Great Britain (Walker et al., 2008). Newspapers often report poisoning of domestic animals (especially dogs) through rodenticides (Mischke, 2004), but to our knowledge there is no systematic collation or analysis of such reports.

The Scientific Committee on Emerging and Newly Identified Health Risks has conducted an assessment of the potential impacts of biocide use on resistance of nosocomial, community-acquired and foodborne pathogens to antibiotics. This study concluded that some resistance mechanisms are common to both biocides and antibiotics. In particular, the use of triclosan, chlorhexidine, and quaternary ammonium compounds was linked to the development of resistance to antibiotics. To address these concerns an urgent need is identified for quantitative data on exposure to biocides, standards and methods to evaluate the ability to induce/select for resistance, and environmental studies on resistance and cross-resistance to antibiotics following use and misuse of biocides (SCENIHR, 2009).

4.3 Environmental benefits of biocide application

When considering a reduction in the risks to health and environment, the benefits from the use of biocides should be kept in mind. The COWI study concluded that the reduction of risks from the use of biocides should not be at the expense of a reduction of or change in use of biocides which could lead to new sorts of health and welfare problems. Only the problem of superfluous, thoughtless or misplaced use of biocides leading to unnecessary residual and waste products and thereby to unacceptable environmental and health problems, should be considered (COWI, 2009).

The benefits of biocide use are most often discussed in the context of the protection of human health from infectious diseases (Umweltbundesamt, 2006), but environmental benefits can also be postulated.

The economic, environmental and social benefits of plant protection products in agriculture have been assessed by Eyre Associates (2007), with the main emphasis on the economic aspects. The central assumption of the analysis was that the benefits can be deduced from a comparison of standard PPP application with integrated and organic systems. The environmental benefits of PPP have been attributed to land use i.e. based on estimates of the amount of extra land that would be needed to produce the same amount of each product after a complete switch to organic production and the potential increase of fertilisers. However, it is recognised that the drawbacks of the study include the limited data available as well as a considerable uncertainty about the reliability of assumptions. A similar approach might also be usefully adapted and applied to the estimation of the benefits from biocides, although this issue was not seen as a major goal of the project.

A critical review of the use, safety and benefits of microbiocides used in medical devices has been undertaken by Sattar (2006). The review focuses on suitable efficacy testing methods to allow for the selection of the best combination of microbiocides, mode of application and definition of the contact time etc.

The problem of the distribution of invasive animals and plants through ballast water from ships has been known for several decades and has led to the International Convention for the Control and Management of Ships' Ballast Water and Sediments, which was adopted in 2004. The use of biocides (in-situ generation or addition) to prevent or reduce this problem may therefore have benefits for biodiversity, benefits which may also apply to antifouling paints used to prevent marine organisms being transported attached to ships (IMO 2007).

5 Conclusions

The literature research indicated that quantitative data on the production and use of biocides, as well as monitoring data in the environment, which could be used as indicators for observing progress in sustainable use are scarce. The contribution of different emission sources from multiple uses of a range of active substances controlled under several regulatory structures has resulted in a high level of uncertainty about which application areas are most relevant when assessing impacts on the environment. Existing lists of priority substances do not specifically consider biocides, and systematic attempts to prioritise biocides as potential pollutants and to include some of them into monitoring programmes are missing.

The behaviour of biocides in WWTPs is considered as one important criterion for prioritizing active substances relevant for the environment. In this context it is interesting to note that the current strategy for the evaluation of plant protection products according to Directive 91/4134/EEC, based on consideration of the retention and binding of pesticide residues (bound and unextractable residues), has been questioned by experts. They argue that complete biodegradation (mineralization) should also be considered when evaluating active substances. To date a plant protection product which is more than 5% biodegraded in 100 days is accepted if less than 70% bound residues prevent leaching to water bodies (Stieber et al., 2007).

The COWI study concluded that only 105 of the 350 substances for review under the Biocidal Products Directive are classified as dangerous substances and are also included in Annex I to Directive 67/548/EEC (now included in Regulation (EC) No. 1272/2008). For the remaining 245 substances no information on inherent properties, classification and labelling is easily available[15]. These data gaps on active substances will be closed during the implementation of the BPD and following the submitting dossiers as required under Article 5.

The collection and analysis of data on the consumption and application of biocides and monitoring of these compounds in the environment would provide a method for

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[15] Not surprisingly the overall conclusion was that the majority of the active substances can be expected to be toxic or very toxic to aquatic life and that half of the substances are not easily biodegradable. Pest control active substances showed the highest degree of environmental toxicity.

identifying major impacts and for improving the sustainable use of biocides. Both the COWI and the SCENIHR studies concluded that environmental monitoring programmes for undesirable substances should include biocides (COWI 2009, SCNIHR 2009).

Available data from monitoring of biocides suggest that prioritisation of the active substances to be included in monitoring programmes should be carried out on a scientific basis, using consumption data and the intrinsic properties of the active substances such as adsorption behaviour, volatility and biodegradability.

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Annex 1: Comparison of BPD and PPP Review Programmes

Active substances included in the Review Programme of the BPD	
In or pending PPP Review	**Not in PPP Review**
Cyproconazole, Deltamethrin, Cypermethrin, Cyfluthrin, alpha-Cypermethrin, Flufenoxuron, Tebuconazole, Imidacloprid, Propiconazole, Imazalil, Pyriproxyfen, Difenacoum, Bromadiolone, Etofenprox, Aluminium phosphide, Bacillus thuringiensis, Benzoic acid, Captan, Carbendazim, Carbon dioxide, Chlorothalonil, Chlorotoluron, Copper dihydroxide, Copper oxide, Copper sulphate, Copper thiocyanate, Copper(II)carbonate copper(II) hydroxide (1:1), Cyanamide, Bifenthrin / Biphenate, Dazomet,Tolylfluanid, Didecyldimethylammonium chloride, Ethanol, Fenoxycarb, Fipronil, Fluometuron, Metam-sodium, Mixture alpha-cyano-3-phenoxybenzyl, Acetamiprid, Folpet, Chlorophenylaminocarbonyl-difluorobenzamide, N-cyclopropyl-1,3,5-triazine-2,4,6-triamine, Pyrethrins and Pyrethroids, Sodium hypochlorite, Spinosad, Sulphuryl difluoride, Terbuthylazine, Thiabendazole, Thiamethoxam, Thiram, Trimagnesium-diphosphide, Warfarin, Warfarin sodium, Ziram	Rotenone, Hexaflumuron, Difethialone, Chlorfenapyr, Brodifacoum, Hydramethylnon, Alkyl-benzyl-dimethylammonium chloride, Ammonium sulphate, Bacillus sphaericus, Bendiocarb, Boric acid, Bronopol, Chloralose, Chlorophacinone, Coumatetraly, Diazinon, Dichlofluanid, Dichlorophen, Dichlorvos, Disodium octaborate tetrahydrate, Diuron, Fenitrothion, Formaldehyde, Formic acid, Hydrogen peroxide, L-(+)-lactic acid, Methylene dithiocyanate, Flocoumafen, Monolinuron, Permethrin, Nabam, Naled, Nitrogen, Peracetic acid, Propoxur, Benzylalkyldimethyl (C8-C22)chlorides, bromides, or hydroxides), Azamethiphos, Silver nitrate, S-Methoprene, Sodium dimethylarsinate, Sodium dimethyldithiocarbamate, Terbutryn, Tetramethrin, Zineb
N=58	**N=44**

Annex 2: Consumption of selected biocidal substances used as washing and cleaning agents in Germany (year 2004)

substance	CAS	Disinfection				Bleaching				Preservation			
		CH	TH	FB	CS	CH	TH	FB	CS	CH	TH	FB	CS
		t/a	t/a	t/a	t/a	t/a	t/a	t/a	t/a	t/a	t/a	t/a	t/a
2-Propanol	67-63-0	254,4	0,0	5,2	2,8					0,5	0,0	0,0	0,6
sodium hypochlorite	7681-52-9	94,0	86,6	19,7	88,1	1934	251,9	54,8	389,0				
Alkyldimethylbenzyl ammonium chloride (QAV C12-C18)	68391-01-5	134,2	208,2	3,4	96,8					0,6	39,8	0,3	1,7
5-Chloro-2-methyl-4-isothiazolin-3-one / 2-Methyl-4-isothiazolin-3-one (mixture CMI/MI)	26172-55-4 / 2682-20-4	1,0	0,9	1,4	0,5					592,7	307,1	58,7	328,0
Benzoic acid (including benzoates)	65-5-0	1,4	6,6	1,6	1,4					96,5	27,4	4,3	13,8
Glutaraldehyde	111-30-8	13,3	0,0	1,0	50,0					69,2	85,3	4,6	0,4
Dichloroisocyanuric acid sodium salt	2893-78-9	2,4	0,0	0,0	5,0	22,4	0,0	0,0	5,6				
1,2-Benzisothiazolin-3-one	2634-33-5	0,1	0,0	0,0	0,0					81,2	156,2	27,2	7,0
2-Phenoxyethanol	122-99-6	7,8			0,0					7,8	1,2	51,3	0,2
2-chloroacetamide,	79-07-2	0,0	0,0	1,3	0,1					5,7	8,7	17,0	0,6
Formaldehyde	50-00-0	4,3	0,8	1,8	213,3					8,6	2,9	3,8	0,2
Trichloroisocyanuric acid	87-90-1	0,0	0,0	0,0	0,0	5,2	0,0	0,0	0,0				
H_2O_2	7722-84-1	2,9	0,0	0,0	177,5	34,4	2103	0,0	270,7				
Triclosan	3380-34-5	1,1	0,0	0,0	0,5					1,8	0,0	0,0	0,1
2-Bromo-2-nitro-1,3-propanediol (Bronopol)	52-51-7	0,0	0,0	0,6	0,0					338,8	46,8	3,1	3,0

CH: Cleaning in private homes
TH: Textile cleaning in private homes
FB: Floor cleaning (private homes and business)
CS: Cleaning of sanitary panels (private homes and business)

Annex 3: Comparison of biocidal active substances with the IKSR list of Rhine River relevant substances

Name	CAS	PT*)
1,4-dichlorobenzene	106-46-7	-
Copper	7440-50-8	2, 4, 5, 11, 21
Zinc	7440-66-6	-
Dibutyl phthalate	84-74-2	-
Bis(tributyltin) oxide	56-35-9	-
Chlorpyrifos	2921-88-2	-
Chlorotoluron	15545-48-9	6, 7, 9-13
Coumaphos	56-72-4	-
Dichlorvos	62-73-7	18
Dicofol	115-32-2	-
Dimethoate	60-51-5	-
Diuron	330-54-1	6, 7, 10
Endosulfan	115-29-7	-
Fenitrothion	122-14-5	18
Fenthion	55-38-9	
Hexachlorocyclohexane	608-73-1	-
Lindane	58-89-9	-
Isoproturon	34123-59-6	6, 7, 9-13
Malathion	121-75-5	-
Methoxychlor	72-43-5	-
Monolinuron	1746-81-2	2
Pentachlorophenol	87-86-5	-
Phoxim	14816-18-3	-
Simazine	122-34-9	-
Trichlorfon	52-68-6	-
Chlorocresol	59-50-7	1-4, 6, 9, 10, 13
Naphthalene	91-20-3	19

*) “-“: Identified active substances not included in the Review Programme

Source: http://www.iksr.org/uploads/media/Bericht_Nr._161d_01.pdf

Annex 4: Consumption of cooling water biocides in European countries (data in kg/a on a substance basis)

	Active substance	UK 1)	NL 1)	F	D 2)
oxidative biocides					
Chlorine based	Chlorine				184.000
	Sodium hypochlorite	731.000	2.100.000	817.000	674.000
	Calcium hypochlorite				146.000
	Sodium dichlorisocyanuric acid	19.300			10.000
	Chlorodioxide	13.000			
Bromine based	Sodium bromide	356.000			
	1-Brom-3-chlor-5,5-dimethylhydantoin (BCDMH)	286.000			1.830.000
	Sodium hypobromite				44.000
	Ozone	0			3.000
	Hydrogen peroxide	910			1.180.000
	Potassium peroxymonobisulfate				11.000
	Peracetic acid	975			50.000
Total amount of oxidative biocides		1.407.185	2.100.000	817.000	4.132.000
non-oxidative biocides					
QAV	Dimethylcocobenzyl-ammonium chloride	23.400			
	Benzylalkylammonium chloride	21.400			
	Total amount of QAV	71.152			64.100
Isothiazolinones	5-Chlor-2-methyl-4-isothiazolin-3-on	13.200			
	Total amount of Isothiazolinones	18.000	2.250		20.800
	halogenated Bisphenols (Dichlorophen, Fentichlor)	12.150			
	Thiocarbamate	56.800			
Others	Glutardialdehyde	56.400	15.000		
	Tetraalkylphosphoniumchloride	9.500			
	2,2-Dibromo-3-nitrilo-propionamid	17.200	10.000		19.800
	2-Bromo-2-nitropropan-1,3-diol				400
	S-Triazine				11.000
	Dodecylguanidinehydrochloride				6.900
	Methylenbisthiocyanate (MBT)	2.270			2.400
	ß-Bromo-ß-nitrostyrene	231			
	Fatty amines 3)			20.000	
	Others	4.412			
Total amount of non-oxidative biocides		248.115	27.250	20.000	125.400

Reference:

UK, **F**: IPPC Reference Document on the Application of BAT to Industrial Cooling Systems (11/2000)

NL: IKSR Synthesebericht Antifoulings und Kühlwassersysteme (Entwurf 15.11.2001)

D: This study (F+E 200 24 33, Januar 2001)
1) All cooling water systems
2) Only recirculation cooling systems, NaOCl is indicated as Cl_2
3) Consumption of fatty amines in a costal power plant

Source: Gartiser et al. (2002)