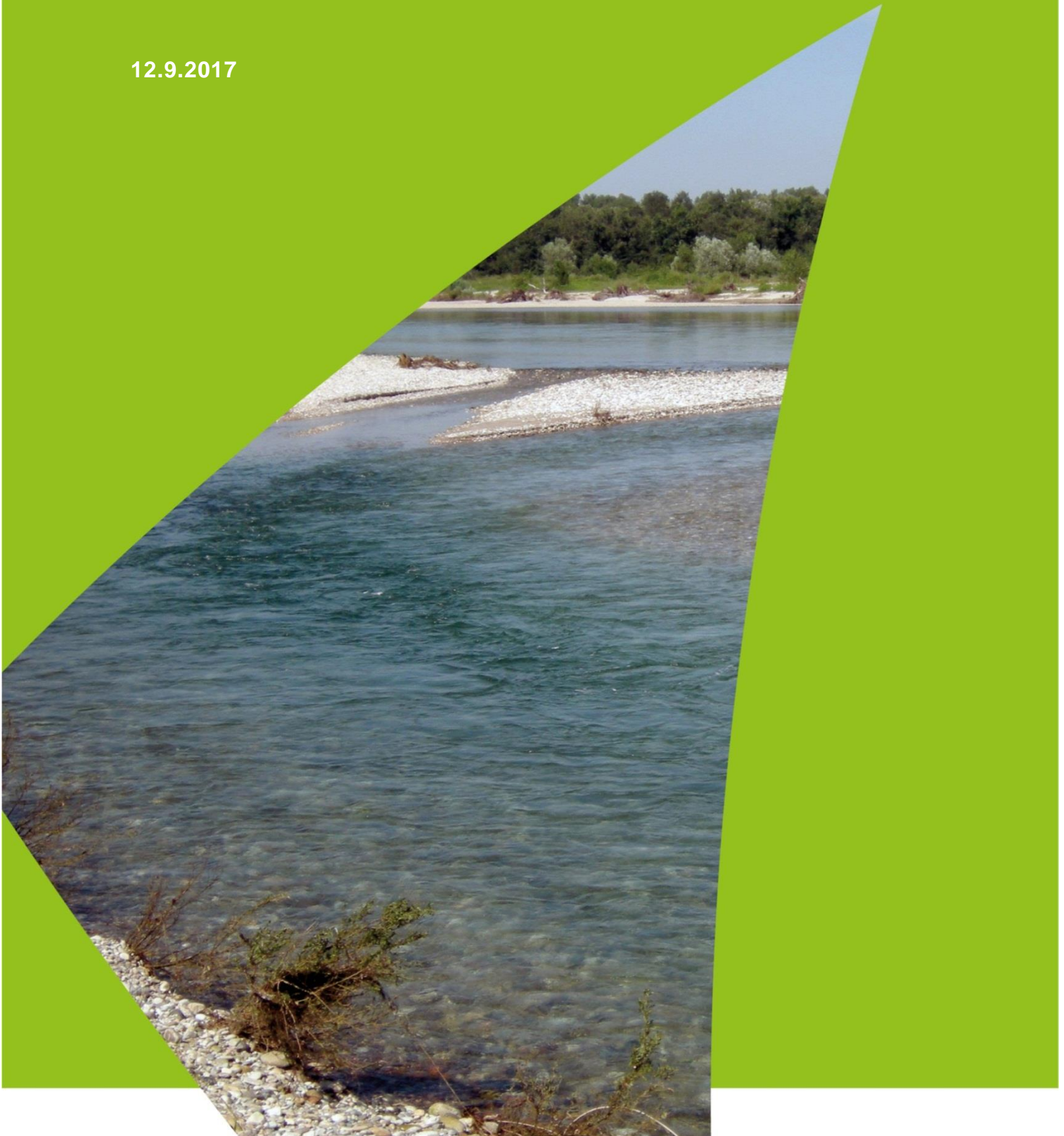


The occurrence of 12 EU priority substances in Swiss surface waters and biota – a review of monitoring data

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Note

The analyses contained in the report were conducted up to April 2014 and reflect the available data and EU Water Framework Directive Environmental Quality Standard approaches that were in use at that time.

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Summary

In 2000 the European Union set up the Water Framework Directive (WFD) to protect all surface and ground water resources. An integral management tool within the WFD is the implementation of environmental quality standards (EQS) for priority substances. An EQS value represents the concentration of a chemical that should not be exceeded to prevent adverse effects. Three types of EQS values are used: 1) an annual average EQS (AA-EQS), to protect against long-term effects; 2) a MAC-EQS, meant to protect against short-term effect of a maximum allowable concentration (MAC); 3) a biota-EQS, to protect against indirect effects and secondary poisoning. A first list of EQS values for 33 substances was adopted in 2008. In 2013 the EU added 12 additional substances to this list.

EQS values are not only generated for EU priority substances. Individual EU member states generate EQS values for a large number of compounds that have been prioritised according to national guidelines. Within the WFD, these compounds are referred to as river basin specific pollutants. In Switzerland, the Ecotox Centre already established EQS values for more than 60 such compounds.

One objective of this report is to derive EQS values for five pharmaceuticals. The main aim of this report is to summarise the exposure situation in Switzerland regarding the 12 new priority substances and the five pharmaceuticals (using available data up to April 2014¹). Measured concentrations of the compounds were extracted from a national database (the MicroPoll database) and searched in the literature. In addition, exposure data from other European countries were collected and compared with Swiss exposure data. When sufficient concentration data were available for a compound, these concentrations were compared with EQS values to evaluate the probability of EQS exceedance. Finally, compounds were identified for which current monitoring data chemical analytical techniques are not satisfactory.

The available data for the 17 compounds are very heterogeneous in terms of their quality, quantity and regional distribution. Nonetheless, three main conclusions can be formulated. First, chemical analysis needs to be improved to bring limits of quantification below EQS values. For some compounds this goal is within reach (PFOS, bifenox, cybutryne), for others it will remain a challenge (dicofol, cypermethrin, dichlorvos, HBCD, heptachlor). This conclusion is supported by data from adjacent countries, particularly Germany and France. Second, more water and biota monitoring is required. This involves more sampling as well as a better regional distribution of sampling. Third, although the exposure data is not comprehensive or conclusive, the risk posed by the 17 compounds can be classified as: not existent, low, medium, unknown and high. The conclusions are as follows:

- the five pharmaceutical for which EQS values were derived have a risk probability that is low (ciprofloxacin, propranolol) or negligible (irbesartan, valsartan, metformin)
- the risk appears low for dicofol and dichlorvos and is medium for terbutryn
- for lack of data, the risk posed by quinoxifen, aclonifen, bifenox, cypermethrin, HBCD and heptachlor is classified as “unknown”
- for three priority substances, the risk is high: PFOS, dioxin like PCBs and cybutryne
- a number of compounds require additional monitoring: quinoxifen, aclonifen, bifenox, PFOS and to a lesser extent this also applies to ciprofloxacin
- PFOS, dioxins and dl-PCBs, HBCD, heptachlor have been banned but are of long term risk due to their persistence, continued releases from landfills and presence in sediments

¹ In 2015, a six month monitoring campaign was conducted in five small Swiss catchments. More than 200 compounds were analysed, including some of the 12 additional EU EQS substances (see Doppler et al., 2017). A similar study is underway in 2017, again covering five small Swiss catchments. Data from these studies were not considered / are not yet available.



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1 Background to the Water Framework Directive and EU prioritization process

1.1 The Water Framework directive

In 2000 the EU set up the Water Framework Directive (WFD) as a comprehensive tool for the monitoring and protection of the European aquatic environment. The main focus of the WFD is on surface water quality but the WFD has a broader scope and also covers issues such as groundwater, drinking water and flooding and droughts (WFD, 2013). To regulate water quality (chemical status), the WFD makes use of compound specific environmental quality standards (EQS). These EQS values are calculated for selected compounds (so called priority substances) and reflect maximum concentrations that are deemed to pose a tolerable risk for organisms in the aquatic environment and prevent acute and long-term effects. As part of the WFD, the chemical status of European water bodies has to be determined by means of water sampling as well as biota sampling followed by chemical analysis. In addition, management plans have to be developed to ensure that protection goals are being met and a good chemical and ecological status can be assured.

1.2 EU priority substances

The prioritisation of substances for which EQS are derived follows a review process and focuses on compounds predicted to pose the greatest risk to the EU-wide aquatic environment. First, for a large number of compounds, exposure and hazard is estimated using available modelled and measured exposure data as well as ecotoxicological data. Ecotoxicological data include, for example, information on PBT (persistent, bioaccumulative and toxic) and CMR (carcinogenic, mutagenic and reprotoxic) properties of compounds. Second, a short-list of substances is proposed and substance dossiers are prepared. EQS values are derived from available toxicity data and following a harmonized derivation procedure (Commission, 2011); already established EQS values can be reviewed and revised. Third, in most cases these substances then reach the final list of substances included in a Commission's proposal. However, some substances do not progress through all the steps in prioritisation for a number of reasons. These reasons can be: a substance is not considered to represent an EU-wide problem; its prioritisation on the basis of one information source is not supported by other sources; or, there is insufficient toxicity or exposure information to reliably determine the risk posed by a substance. Beyond these technical aspects there are other factors that influence the selection. These factors include: the cost-benefit analysis of listing one or more substances; the manageability of the list; and also political views. All these aspects may influence the final choice of substances for which EU-EQS values are finally adopted.

In 2008 a first set of 33 EQS values were published (Commission, 2008b). In 2013 a new set of 12 compounds was added to the set of 33 (see Table 1; Commission, 2013). Furthermore, modifications were made to the EQS values of 10 of the initial 33 compounds (Commission, 2013) and a watch list was set up to support the EU prioritisation process. This watch list is a new prioritisation tool to improve the EU wide exposure assessment of candidate substances. Thus, in the EU Directive 2013/39/EU (Commission, 2013), diclofenac, 17 β -estradiol and 17 α -ethinylestradiol were put on the watch list to increase monitoring data and in this way facilitate future risk assessment for these compounds.

In addition to the EQS values for EU priority substances, many EU Member States have developed national sets of quality criteria for river basin specific pollutants (RBSPs) according to national prioritisation schemes and using the EQS approach. For example, in Switzerland, the Swiss Centre for Applied Ecotoxicology has derived more than 60 environmental quality criteria for such RBSPs that enter rivers and lakes from point and non-point sources (Oekotoxzentrum, 2014).



1.3 Aim of the report

The main objective of this report is to review the Swiss exposure data and evaluate risks of possible EQS exceedance with respect to the 12 new EU priority substances and five additional compounds (RBSPs; see Table 1). These five additional compounds were prioritised according to the evaluation concept of FOEN (Swiss Federal Office of the Environment) and complement the list of RBSP for which EQS values already exist (see section 1.2). The evaluation concept of FOEN is based mainly on exposure criteria, like frequency of detection and concentration, but also includes hazard information (Kase et al., 2011). The objective separates into four aims: 1) derive EQS values for the five selected compounds; 2) summarise the information on concentrations and exposure levels for these five compounds and the 12 new EU priority substances in the Swiss aquatic environment; 3) perform a risk assessment by comparing concentrations in water and biota with EQS values, and 4) identify information gaps and requirements and possibilities/recommendations for future monitoring.

The review mainly makes use of a national database, information available in the scientific literature or information that was obtained through communication with national and international experts. To be comprehensive, this review also compares observations from Switzerland with monitoring data from neighbouring countries. Information from databases and literature were compiled **up to April 2014** – unless stated otherwise, all analyses in the report reflect the available information up to that time.

Table 1: Basic properties of the 17 compounds that are reviewed in this report, 12 new EU priority compounds and five pharmaceuticals considered for environmental quality standard (EQS) derivation as river basin specific pollutants (RBSP) in Switzerland

Twelve new EU EQS compounds	Name of substance	CAS	Application	Use forbidden
34	Dicofol	115-32-2	organochlorine pesticide	yes
35	PFOS ^a	1763-23-1	industrial chemical	yes
36	Quinoxifen	124495-18-7	fungicide	no
37	Dioxin (and dioxin like compounds)	1746-01-6	industrial chemical / undesired waste product	yes
38	Aclonifen	74070-46-5	herbicide	no
39	Bifenox	42576-02-3	herbicide	no
40	Cybutryne (Irgarol)	28159-98-0	biocide / algaecide	limited use
41	Cypermethrin	52315-07-8	pyrethroid insecticide	no
42	Dichlorvos	62-73-7	insecticide	yes
43	HBCD 10 ^b	25637-99-4	flame retardant	yes
	HBCD 11			
44	Heptachlor	76-44-8	insecticide	yes
	Heptachlor epoxide	1024- 57-3		
45	Terbutryn	886-50-0	herbicide	no
Five new Swiss RBSP	Name of substance	CAS	Application	Use forbidden
1	Irbesartan	138402-11-6	pharmaceutical	no
2	Valsartan	137862-53-4	pharmaceutical	no
3	Ciprofloxacin	85721-33-1	pharmaceutical	no
4	Propranolol	525-66-6	pharmaceutical	no
5	Metformin	657-24-9	pharmaceutical	no

a: perfluorooctane sulfonate; b: hexabromocyclododecane



2 Exposure and risk assessment of 12 new EU priority substances and five pharmaceuticals for Switzerland

2.1 MicroPoll database

A large set of chemical concentration measurements in surface waters and effluents in Switzerland is available in the form of a database (see Munz et al., 2012; Göggel et al., 2013). Information in this “MicroPoll database” originates from a variety of sources such as national and cantonal sampling and measurement campaigns. The database was the main source of information used to explore the exposure of Swiss surface waters to the set of 17 chemicals of interest. For the purpose of this review, the interpretation of surface water concentrations is straightforward. However, also concentrations in effluents can be evaluated in a surface water context by applying, for example, a 10-fold dilution factor of effluent in surface water (Goetz, 2013). It has to be considered though, that this does not apply to small rivers under conditions of drought where dilution may become negligible or in larger rivers, where dilution may be much larger.

Of the 17 compounds under investigation, not all appear in the database. Dioxins and hexabromocyclododecane (HBCD) are not listed; dicofol is listed in the database, but there are no entries for either surface or waste waters; bifenoX is not listed in the database, but a few measurements occur for its metabolite, bifenoX acid. Furthermore, there are two aspects that complicate analyses of the data. First, for the compounds that are listed in the database, the data often tend to be associated with a single or a few sampling locations. Second, not all analyses are associated with a limit of quantification (LOQ). When a compound is not detected, it is thus not always clear what the maximum possible concentration could be.

The issue of interpreting data that are below the quantification limit can be dealt with in various ways. To present distributions, or to calculate averages or medians, data below LOQ can be assigned a value of half the LOQ (e.g. UBA, 2009), or they can be assigned the value of the LOQ itself (e.g. Müller, 2011). In this report we do not numerically interpret data below LOQ. We focus on “detects” and “measured values” and we calculated averages and distributions only with data that have been assigned a numerical value in the database. This approach is analogous to previous studies that have made use of the MicroPoll database (e.g. Götz et al., 2010a). However, to be comprehensive, we count and plot the number of undetects.

The available data from the MicroPoll database are summarised in Table 2. The format of the table, showing the number of detects over the number of samples analysed and a summary of concentration information, follows that of earlier studies (e.g. Götz et al., 2010a; Götz et al., 2010c; see also Kase et al., 2011). One straightforward and important conclusion that can be drawn from the table is that the LOQs of six of the 12 new EU priority substances are below the AA-EQS value. Thus, effective monitoring for many compounds is hampered due to the limits posed by chemical analysis.



Table 2: Summary of data extracted from the MicroPoll database (revision date: 24.02.2012)

No. ^a	Name of substance	AA-EQS (ng/L)	MAC-EQS (ng/L)	Biota-EQS (ng/kg)	Typical LOQ (ng/L) ^b	River water # Detects / # Measurements	River water average concentration (ng/L)	River water 90% concentration (ng/L)	River water median concentration (ng/L)	WWTP ^c effluent # Detects / # Measurements	WWTP effluent average concentration (ng/L)	WWTP effluent 90% concentration (ng/L)	WWTP effluent median concentration (ng/L)
34	Dicofol	1.3	n/a	33'000	-	no entries	-	-	-	no entries	-	-	-
35	PFOS	0.65 / 230 d	36'000	9'100	5	27 / 98	15	37	9	26 / 76	179	503	79
36	Quinoxlyfen	150	2'700	-	-	no entries	-	-	-	no entries	-	-	-
37	Dioxins	n/a	n/a	6.5	-	no entries	-	-	-	no entries	-	-	-
38	Aclonifen	120	120	-	10	19 / 183	193	481	40	no entries	-	-	-
39	Bifenox (acid)	12	40	-	3-100	0 / 12	-	-	-	0 / 6	-	-	-
40	Cybutryne (Irgarol)	2.5	16	-	5-10	277 / 7144	20	48	10	22 / 103	104	422	8
	RÜS Weil am Rhein ^e					42 / 3683	6	8	5	n/a	n/a	n/a	n/a
	Rest					235 / 3458	22	50	10	n/a	n/a	n/a	n/a
41	Cypermethrin	0.08	0.6	-	5-50	7 / 5829	67	160	50	0 / 53	-	-	-
	RÜS Weil am Rhein				5	0 / 1796	-	-	-	n/a	n/a	n/a	n/a
	Rest				10-50	7 / 4033	67	160	50	n/a	n/a	n/a	n/a
42	Dichlorvos	0.6	0.7	-	5	1 / 3999	21	21	21	no entries	-	-	-
	RÜS Weil am Rhein					1 / 3830	21	21	21	n/a	n/a	n/a	n/a
	Rest					0 / 169	-	-	-	n/a	n/a	n/a	n/a
43	Hexabromocyclododecan	1.6	500	167'000	-	no entries	-	-	-	-	-	-	-
44	Heptachlor and epoxide	0.0002	0.3	6.7	2	0 / 119	-	-	-	no entries	-	-	-
45	Terbutryn	65	340	-	5-10	1386 / 12654	21	40	10	79 / 162	352	1510	30
	RÜS Weil am Rhein					461 / 6185	5	6	5	n/a	n/a	n/a	n/a
	Rest					925 / 6469	30	60	14	n/a	n/a	n/a	n/a
	Irbesartan	704'000	19'100'000	-	10	93 / 145	41	76	16	no entries	-	-	-
	Valsartan	560'000	9'000'000	-	one LOQ=5	69 / 70	34	57	32	6 / 6	1345	4208	260
	Ciprofloxacin	89	363	-	20	6 / 80	34	53	28	9 / 9	294	590	210
	Propranolol	160	12'000	-	10	66 / 478	18	55	13	18 / 22	86	193	67
	Metformin	1'000'000	9'100'000	-	10	335 / 439	362	540	81	6 / 6	10347	14779	10530

- a EU EQS priority substance number, see Table 1
b limit of quantification reported for most measurements.
c waste water treatment plant
d the EU EQS (0.65 ng/L) is a back-calculated concentration from the biota-EQS; 230 ng/L is the AA-EQS derived by the Ecotox Centre
e Rhine monitoring station at Weil am Rhein
n/a = not applicable
- = no information

Several new EQS values are biota based². As the MicroPoll database does not contain information on biota, data on concentrations of the relevant substances in biota were searched in the literature. In addition to a broader literature review on aqueous and biota concentrations, several experts were contacted – scientists that deal with monitoring data – to provide for up-to-date information on the various compounds.

2.2 Information on exposure data from neighbouring countries, literature sources and expert feedback

Given the fact that the MicroPoll database is not fully comprehensive with respect to the studied compounds, and also for the purpose of comparison, information on exposure was obtained from neighbouring countries, particularly Germany, France and The Netherlands. This occurred in the form a literature review covering the period up to April 2014. Typical data sources in this respect were reports by water works such as RIWA (Vereniging van Rijnwaterbedrijven) and ARW (Arbeitsgemeinschaft Rhein-Wasserwerke) and data tables from the ICPR (International Commission for the Protection of the Rhine) and the EU.

A summary of the chemical monitoring situation in Germany is shown in Figure 1 (Arle et al., 2014). From this figure, it is clear that a large number of the new EQS-compounds have monitoring problems in that the LOQs are too high to determine if EQS-values are being met (indicated by the grey bars in Figure 1). This confirms the information for Switzerland shown in Table 2, where the LOQs exceed the AA-EQS for many compounds.

² In April 2014, the situation shown in Table 1, biota EQS values in µg/kg were back-calculated to aqueous AA-EQS values. This is no longer applied in EU water quality monitoring. This report was not updated to reflect this change in approach.



Germany: LAWA monitoring stations

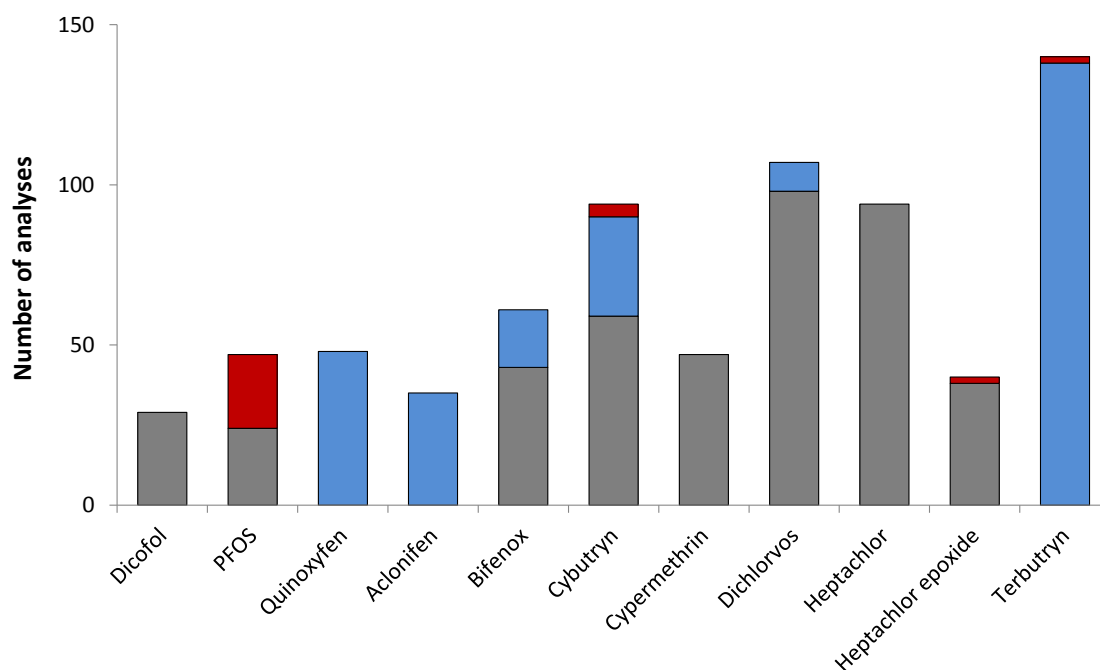


Figure 1: The number of LAWA (Länderarbeitsgemeinschaft Wasser) monitoring stations for which the annual average concentrations for the period 2009-2011 was either below (blue) or above the AA-EQS (red) of 10 new EU priority substances. When the LOQ exceeded the AA-EQS, the data are labelled in grey (adapted from Figure 48 in Arle et al., 2014).

The EU provides some 90th percentile information from monitoring data for new priority compounds (Commission, 2010). However, these data are not comprehensive in that only a single value is listed for each compound and sometimes there are only data for a single EU country (Commission, 2010). To improve on this situation, the EU Joint Research Centre (JRC) at Ispra is developing an environmental information system to collect and process EU wide monitoring data (IPChem, Integrated Platform for Chemical Monitoring; see “Sub Objective 2.2” in IPChem, 2014). This database is not yet available but may be based on “Empodat”, a database with monitoring data from NORMAN (2013). NORMAN is a network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances (<http://www.norman-network.net/>). Data from Empodat was extracted and collated in a similar format as Table 2 (see Annex Table 1). This table also includes information from French monitoring campaigns conducted from 2007-2010. Information from France was provided by CEP (Expert Prioritisation Committee, France, 2013).

To visualise the quantity and the quality of the data that is available internationally, the Swiss, the French and the Empodat data are plotted in Figure 2 in the same way as the German data shown in Figure 1. Although the data density varies considerably across the four data sets, it is clear that the issue of insufficient analytical capabilities – high LOQs for various compounds – is a general phenomenon (i.e. grey areas for the same compounds).

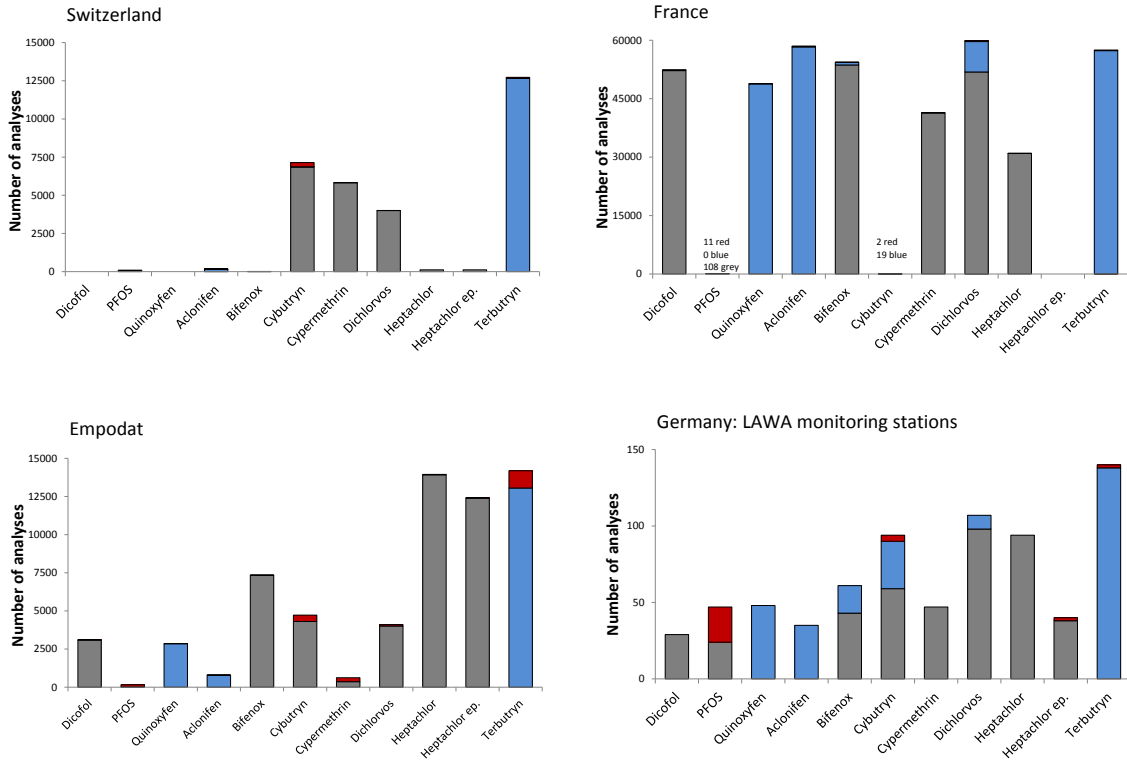


Figure 2: Distribution of the analyses of 10 new EU priority substances that were either below (blue) or above the AA-EQS (red). When the LOQ was higher than EQS, the data are labelled grey. Data are derived from four sources, Switzerland (MicroPoll database; top left), France (provided by CEP, Expert Prioritisation Committee, France, 2013; top right), NORMAN (Empodat database; bottom left). For Germany (Arle et al., 2014; bottom right; see also Figure 1), the data reflect the distribution of LAWA (Länderarbeitsgemeinschaft Wasser) monitoring stations, for which the annual average concentrations for the period 2009-2011 fell into the blue, red or grey categories.

2.3 Evaluating and classifying the risk of EQS exceedance

Data from the MicroPoll database were compared with the EQS values and – provided sufficient data are available – classified into six groups according to the evaluation scheme developed by Götz et al. (2010a; see also Kase et al., 2011). Environmental concentrations below the EQS are classified as good or very good – when concentrations are more than 10-fold below the EQS. Environmental concentrations above the EQS are classified from moderate through insufficient to poor (Table 3).

Table 3: Summary of data extracted from the MicroPoll database (revision date: 24.02.2012)

Evaluation	Description	Compliance with AA-EQS
Very good	The EC is 100 times lower than the AA-EQS	AA-EQS is met
	The EC is 10 times lower than the AA-EQS	
Good	The EC is lower than the AA-EQS	AA-EQS is exceeded
Moderate	The EC is lower than twice the AA-EQS	
Insufficient	The EC is between 2- and 10-fold the AA-EQS	
Poor	The EC is higher than 10-fold the AA-EQS	



2.4 Surface water and biota concentrations – exposure, risk and recommendations

In this section, exposure data for the 17 compounds is presented and discussed on a substance by substance basis. The order of the compounds follows the numbering of the priority substances (Commission, 2012; see also Table 1). The exposure data is compared against the respective EQS-values to evaluate the risk of EQS exceedance. For each of the compounds, possible information gaps are identified and recommendations are provided.

2.4.1 Dicofol

AA-EQS = 1.3 ng/L

“...Dicofol is an organochlorine pesticide (aracaricide; miticide) that is chemically related to DDT, and used for controlling mites that damage cotton, fruit trees and vegetables...” (Loos, 2012)

Exposure

Dicofol has been banned in Switzerland for more than 10 years (BAFU, 2013b), in the EU it is banned since March 2009 (Commission, 2008a). There are no data on dicofol in the MicroPoll database.

Precise information on the presence of dicofol in rivers in neighbouring countries is limited. This is because LOQs of the employed analytical methods in Germany, The Netherlands and elsewhere are too high to detect the presence of dicofol at environmentally realistic concentrations (e.g. Arle et al., 2014). In recent Dutch reports on sampling in the Rhine catchment (RIWA, 2011; RIWA, 2012), an LOQ of 250 ng/L is listed, which is far above the EQS of 1.3 ng/L. Dicofol was not detected above this high LOQ in 1'313 samples. Also a German study did not find dicofol above a considerably lower LOQ of 10 ng/L (180 samples at 45 locations; Steffen, 2013); the LOQ being 8-fold over the AA-EQS. Oehme et al. (2008) report a lower LOQ (1 ng/L) for a study in the river Elbe; no dicofol was found. LOQs above the dicofol AA-EQS are also apparent in Figure 1. Figure 1 indicates – for 10 new EU EQS compounds – at how many LAWA (Länderarbeitsgemeinschaft Wasser) monitoring stations the annual average concentration was either above (red bar) or below the EQS (blue bar). For Dicofol all data are shown as a grey bar, this indicates that the compound was not detected above the LOQ and that the LOQ is above the AA-EQS (the dicofol data comprise 29 LAWA measuring stations). For France and the Empodat database a similar picture emerges. In both cases, more than 99% of the data have an LOQ that exceeds the AA-EQS, the few remaining data are associated with an EQS exceedance.

Also for biota there is scant information on dicofol. A review of data from the German Specimen Bank indicates that dicofol was not measured in biota (Schudoma and Schröter-Kermani, 2013). Ternes and co-workers (2000) sampled eels in German rivers and also deployed SPMDs (semi-permeable membrane devices; passive samplers for lipophilic compounds). Dicofol was not found in any fish sample (above an LOQ of 40 µg/kg; biota-EQS = 33 µg/kg) but it was identified in SPMDs from one sampling location (150 µg/kg lipid with an LOQ of 10 µg/kg). Although data are currently sparse, a review of analytical detection methods for priority compounds reports that a biota LOQ for dicofol below 10 µg/kg is possible and sufficient for future biota-EQS compliance monitoring (Loos, 2012).

Risk

As no information is available on water or biota concentrations, possible risks cannot be determined. However, when considering the fact that Dicofol has not been used for a long time – one possible current (minor) source of dicofol may be residues on imported fruits (Brändli et al.,



2004 and EFSA, 2011) – its presence in the Swiss aquatic environment is likely not of concern. This is supported by the fact that the compound is not persistent, is easily hydrolysed and has a fairly short half-life (some days; see Buchheim et al., 2005). Consequently, the risk of AA- and biota-EQS exceedance appears low.

Recommendation

To ascertain that dicofol is absent from the aquatic environment, the use of passive sampling would be an option, particularly in areas where dicofol has been used in the past (see Ternes et al., 2000). Given the short half-life of several days under neutral conditions (Buchheim et al., 2005), relevance is low and a targeted sampling campaign is not recommended. However, sampling for dicofol can be combined – at little additional costs – with sampling for other compounds where the same techniques can be applied (e.g. see section 2.4.4. on dioxins and dioxin-like PCBs).

2.4.2 PFOS

AA-EQS = 0.65 ng/L or 230 ng/L³

“...Perfluorooctane sulfonate (PFOS) is a fully fluorinated anion, which is used as such in some applications or incorporated into larger polymers. Due to its surface-active properties it is used in a wide variety of applications e.g. in textiles, and leather products; metal plating; food packaging; fire-fighting foams; floor polishes; denture cleansers; shampoos; coatings and coating additives; in the photographic and photolithographic industry; and in hydraulic fluids in the aviation industry...” (Sweden, 2005)

Exposure

The use of PFOS in Switzerland is not allowed since 2011 (BAFU, 2013b), with an on-going phase out for various use categories. The last phase out period, concerning fire-fighting foams, ends November 2018 (BAFU, 2013c). Waste water is the main source of PFOS to the aquatic environment (Becker, 2008) but also diffuse inputs can play a significant role (Müller, 2011 and Paul et al., 2012). As the compound is being phased out, emissions will reduce over time. Müller (2011) states that, for example in the river Glatt, PFOS concentrations have already noticeably declined (2-3 fold) from 2006 (Huset et al., 2008) to 2009 (Müller, 2011).

There are 98 unique entries in the database for river water, with half the entries coming from two stations on the Rhine (Industrielle Werke Basel, n=27; Weil am Rhein, n=21). The average concentration for all detects is 15 ng/L (Table 1). Additional information is available from WWTP effluents. Based on concentrations found in treated sewage effluent (average 179 ng/L, Table 1) and a dilution factor of 10 (Goetz, 2013), a surface water PFOS concentration range of 10 to 20 ng/L is plausible. This concentration range is further substantiated by observations made in ground water, where PFOS was detected in the range of 10 to 40 ng/L at locations where ground water was affected by treated sewage effluent (Reinhardt, 2010). Finally, in the Rhine (Mainz, Köln and Düsseldorf), PFOS concentrations fluctuate between ca. 5 and 15 ng/L (Brauch et al., 2012; IKSR, 2011b). In general, all these data substantiate the average concentration calculated from the database, however, there are indications of a downward trend. In a Swiss survey (Müller, 2011), covering 27 rivers and 43 sampling locations, PFOS was detected above LOQ in 70 of 77 samples with an average value of 9 ng/L, i.e. just below the average from the database. Two studies from 2013 report river water concentrations in the range of 1 to 5 ng/L (Longrée and Singer, 2013; Longrée et al., 2013), also below the average of the database.

³ The EU EQS (0.65 ng/L) is a back-calculated EU concentration from the biota-EQS; 230 ng/L is the AA-EQS derived by the Ecotox Centre.



When LOQs are listed in the database, they are between 1 and 10 ng/L, typical of what can be achieved according to a review on analytical methods by Loos (2012) but clearly above the AA-EQS of 0.65 ng/L (and below the AA-EQS of 230 ng/L). However, Müller (2011) reports a lower LOQ of 0.46 ng/L and Longrée and Singer (2013) give an LOQ as low as 0.1 ng/L. Figure 1 shows that for monitoring data from Germany and for all 47 LAWA locations the LOQ (grey bar) and/or measured concentrations (red bar) are above the AA-EQS of 0.65 ng/L.

The only biota data for Switzerland concern fish from Lake Constance (Untersee) where an average PFOS concentration of 15 µg/kg was found (IKSR, 2011a), which exceeds the biota EQS of 9.1 µg/kg (Table 2). Analyses from biota in Germany point to a large potential for exceedance of the biota-EQS (94% exceedance in samples from the German Specimen Bank; Schudoma and Schröter-Kermani, 2013). All fish pools from a study conducted in the Rhone exceeded the EQS (Miège et al., 2012). Biota data from The Netherlands also point to: 1) exceedance of the biota-EQS; and, 2) a reduction in PFOS biota concentrations since around the year 2000 (Kwadijk et al., 2010).

Risk

As the LOQs are above the AA-EQS of 0.65 ng/L, it is not possible to effectively determine the risk of the EU AA-EQS exceedance. This both for the water phase and the biota, though downward trends are apparent in data from Switzerland and in data from elsewhere. An exceedance of the MAC-EQS is unlikely.

Given the fact that Müller (2011) already indicates a decline in Swiss PFOS concentrations between 2006 and 2009, it is probable that PFOS concentrations extracted from the database (covering PFOS data from 2007 to 2010) represent an overestimation of current concentrations of PFOS in Swiss rivers. This should be verified, as PFOS may accumulate in sediments.

The available data in the MicroPoll and their classification with reference to both AA-EQS values (see Table 3) are shown in Figure 3.

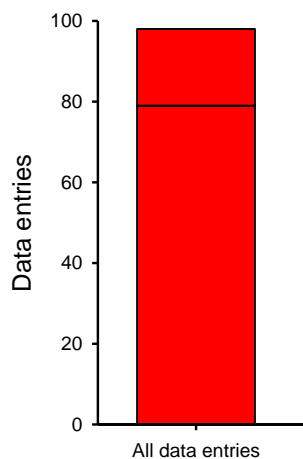


Figure 3: Distribution of PFOS data across five quality classes for the AA-EQS (see Table 3).

Concerning biota, the level of information is unsatisfactory, i.e. a few fish sampled from a part of Lake Constance (Untersee). The available data indicate an exceedance of the biota-EQS by almost a factor of 2. There is thus a large potential for biota-EQS exceedances in catchments where there is a lot of anthropogenic influence and poor dilution of treated sewage effluents. For such catchments, the situation in Switzerland may be similar to that in Germany where 94% of biota samples in the German Specimen Bank exceeded the biota-EQS (Schudoma and Schröter-Kermani, 2013).



Recommendation

Further monitoring of the water phase (and/or sediment) is required to investigate if PFOS levels are indeed decreasing and continue to decrease. To establish spatial trends to locate potential PFOS sources (“Altlasten”), passive sampling can be used as an alternative to traditional water sampling (Kaserzon et al., 2013). Biota need to be monitored so that risks of biota-EQS exceedance can be established.

2.4.3 Quinoxifen

AA-EQS = 150 ng/L

“...Quinoxifen is a protectant fungicide used to control the powdery mildew diseases of wheat, barley, and grapes, and is a potent inhibitor of appressorium formation in these fungi...” (Schirmer et al., 2012)

Exposure

As quinoxifen has applications as a fungicide in agriculture, diffuse inputs to the aquatic environment are expected. However, there are no data in the database, either for surface water or wastewater. Quinoxifen is a hydrophobic compound with a log octanol water partitioning coefficient (logKow) of 4.66 and a very high organic carbon partitioning coefficient (Koc) of 22'929 (Commission, 2003). Therefore, the compound is likely to partition to suspended solids and sediments which will result in low aqueous concentrations. Quinoxifen has been reported in sediments of streams around vineyards (Bereswill et al., 2012) and also in biota (Merli et al., 2010). It was not detected directly in the water phase, for example, in a survey in Germany (North Rhine Westphalia, NRW) from 2012, quinoxifen was not detected above an LOQ of 25 ng/L in 277 samples from 32 rivers (NRW, 2013b) and no EQS exceedances occurred at 48 LAWA sites in Germany (Figure 1). For France, a 90th percentile for quantified measurements of 370 ng/L is given in an EU document (Commission, 2010). However, monitoring data from France – summarised in Annex Table 1 – indicate a very low frequency of detects and also Empodat contains merely one detect in almost 3'000 measurements.

An LOQ of 25 ng/L is sufficient for compliance monitoring and lower LOQs for quinoxifen have been reported (Loos, 2012); thus the LOQ is not a limitation for monitoring (see also Figure 2, where quinoxifen is shown with blue bars).

Recent studies in Germany indicate that quinoxifen can be detected in the water by means of passive sampling (Fernández et al., 2014). Quinoxifen was detected in 38% of the studied agricultural sites (mainly vineyards), sampled during rain events, up to a maximum modelled time-weighted average water concentration of 48 ng/L (Fernández et al., 2014) which is well below the EQS (note that concentrations based on passive sampling are modelled and associated with uncertainties).

Risk

As there are no data on quinoxifen from Switzerland, a risk in terms of EQS exceedance cannot be determined. Particularly regional risks may exist, such as in wine growing areas. However, given the fact that quinoxifen rapidly sorbs to particles and internationally there is a very low frequency of detects (with appropriate LOQs), the risk to the water phase is likely limited but this needs to be established.

Recommendation

It would be helpful to characterise the distribution pattern of quinoxifen in terms of where it is applied and how much is applied. This information can be used to further refine the risk esti-



mate and also help to target a possible monitoring campaign. Given the absence of monitoring data, screening for quinoxifen in areas where its use is known or suspected is advisable. LOQs are low enough to use standard water sampling techniques. As the entry of quinoxifen into the aqueous environment is likely intermittent, passive sampling (or sediment analysis) can be used as a supplementary tool to determine the presence or absence of the compound in the environment (Fernández et al., 2014).

2.4.4 Dioxins and dioxin-like PCBs Biota-EQS = 6.5 ng/kg

“...Dioxins and dioxin-like compounds are chlorinated organic pollutants formed as trace amounts of undesired impurities in the manufacture of other chemicals such as chlorinated phenols and their derivatives, chlorinated diphenyl ethers, and polychlorinated biphenyls and combustion of chlorine containing materials under some conditions...” (Water, 2012)

Exposure

Polychlorinated biphenyls (PCBs) have been banned in Switzerland since 1986 but remain present in the environment. Currently, the main PCB sources to the environment are from redistribution processes, such as long-range atmospheric transport (Ubl et al., 2012) and release from landfills. For dioxins, combustion and incineration processes generate a continuous release.

The database only contains values for indicator PCBs but not dioxins, however, Schmid et al. (2010) recently summarised information on the presence of dioxins and dioxin-like PCBs in the Swiss aquatic environment. Their particular focus was on fish that were sampled between 1990 and 2009. The contribution of atmospheric deposition to exposure of biota can be deduced from data from Swiss alpine lakes where fish have a significant background in terms of toxic equivalents (TEQs) of 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) in the range of 1 to 4 ng/kg (i.e. 60% of the biota-EQS can be reached in “pristine” environments; Schmid et al., 2010). This base level of contamination is typical all across Switzerland. However, there are various locations where the biota-EQS is exceeded considerably. Fish in the Sarine, which is affected by the landfill La Pila, have TEQ levels exceeding 100 ng/kg. Beside known point sources of dioxins and dioxin-like PCBs (e.g. La Pila), the fish survey (Schmid et al., 2010) pointed to unknown PCB sources, for example, along the rivers Birs and the Venoge.

In 2009 a project was initiated by FOEN and various cantons to use passive sampling and sediment analyses to reveal point sources of PCBs. In the project, a PCB source on the Birs could be located and PCB emissions were stopped (Zennegg et al., 2016), work in the Venoge is ongoing (Estoppey et al., 2015). Follow up measurements with passive sampling now show lowered PCB levels in the water phase in the Birs (Markus Zennegg, Empa, personal communication).

Risk

Given the large dataset that is available (Schmid et al., 2010), together with ongoing work (Zennegg et al., 2016), the risk of dioxin-like PCBs expressed as TEQ is well characterised. Some 27% of the fish samples exceeded the biota-EQS of 6.5 ng/kg (Schmid et al., 2010; see Figure 4), particularly eels were affected (e.g. in 2009, 15 out of 16 individuals from the Rhine exceeded the biota-EQS). These data point to an on-going and significant exposure of biota to dioxins and dioxin-like PCBs. In Germany, the previous biota-EQS of 8 ng/kg is exceeded for 52% of the biota, at least for samples from the German Specimen Bank (Schudoma and Schröter-Kermani, 2013). With a reduction of the biota-EQS from 8 to 6.5 ng/kg, it is apparent that a larger proportion than 52% of the biota in the German Specimen Bank exceed the lower biota-EQS.

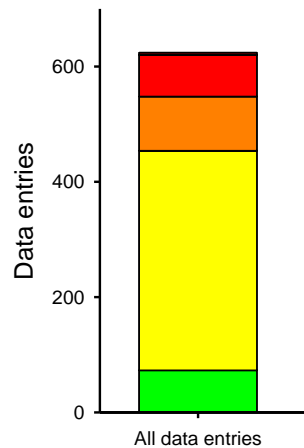


Figure 4: Distribution of dioxins and dioxin-like PCBs data in the biota data set provided by Schmid et al. (2010) across five EQS quality classes (Table 3).

There is a continuing atmospheric input of dioxins and dioxin-like PCBs to the environment that, by itself, leads to a TEQ value that can reach up to 60% of the EQS (e.g. alpine lakes). Besides, there still exist point sources that lead to significant local exceedances of the TEQ that require remediation (e.g. La Pila; Fribourg, 2013). Finally, at locations where sources have been removed (e.g. along the Birs), contaminated sediments will continue to be a source of PCBs for both the water phase and the biota (Hin et al., 2010).

Recommendation

The monitoring practice using passive sampling has proven to be efficient for monitoring spatial and temporal trends of PCBs in water. Thus the method can be used to: 1) locate unknown PCB sources; and, 2) establish if remediation measures have been effective. Passive sampling data can also be used to calculate biota concentrations, as passive sampling mimics bioconcentration Bayen et al., 2009. Such calculations are associated with uncertainties, but they are feasible and represent adequate approximations. Within certain limits and after further development, passive sampling can thus be used to monitor against a biota-EQS.

2.4.5 Aclonifen

AA-EQS = 120 ng/L

“...Aclonifen is intended to be used as a selective pre-emergence herbicide for the control of annual broad-leaved and grass weeds in sunflower...” (Report, 2006)

Exposure

As aclonifen is a herbicide, diffuse inputs to surface waters are expected. There are 183 entries and 19 concentrations listed in the database; 95% of the entries are from sites in the Lake Geneva area and the Rhone. Only 52 of 183 entries are listed with LOQs – which typically lie between 10 and 50 ng/L; only one of the 19 detects is associated with an LOQ. The average concentration is 193 ng/L which is influenced by one very high value, 2318 ng/L; with the highest value excluded the average of the detects is 75 ng/L (the median value is 40 ng/L, Table 2).

In the Netherlands, aclonifen was not detected above an LOQ of 50 ng/L in samples collected along the Rhine in either 2011 or 2012 (RIWA, 2011 and 2012). Also in Germany, no exceed-



ance of the AA-EQS was observed at 35 LAWA locations (Arle et al., 2014; Figure 1) and in 594 samples taken from 106 rivers in NRW aconifen concentrations were always below an LOQ of 25 to 50 ng/L (NRW, 2013b; NRW, 2013a). An absence of detections in Germany and the Netherlands may not be surprising, as for the EU it appears that 70% of aconifen that is used is applied in France and for France the 90th percentile for detects is given as 555 ng/L Commission, 2010 which is close to the 90th percentile value of 481 ng/L in the MicroPoll database (Table 2). Although aconifen is used predominantly in France, Table 1 of the Annex shows a mere ca. 1% detection rate above LOQ for almost 60'000 measurements from France.

Risk

The data base is limited, but three of 183 samples exceeded AA- and MAC-EQS (Figure 5). This points to a local risk in areas where the compound is applied, particularly in terms of MAC-EQS exceedance. The exposure information has a strong regional focus and is limited. The reason for this local focus – the area around Lake Geneva – may be connected to the preferential use of aconifen in France (Commission, 2010).

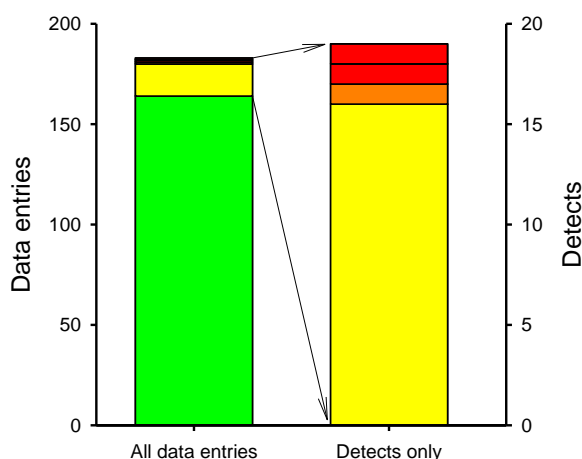


Figure 5: Distribution of aconifen data across five quality classes for the AA- and MAC-EQS (Table 3). Left bar, evaluation of all data entries in the MicroPoll database; right bar, grouping of the 19 detects.

Recommendation

Additional data is needed to provide a more robust data set, particularly when LOQs can be decreased. It appears that detection can be hampered as aconifen does not ionise in ESI-LC-MS/MS (Singer et al., 2009). For future monitoring, it would be helpful to establish where aconifen is used in Switzerland and adapt the monitoring area accordingly.

2.4.6 Bifenox

AA-EQS = 12 ng/L

“...Bifenox is a selective preemergence, preplant soil-incorporated, or postemergence herbicide used to control annual weeds in several crops...” (Ashton et al., 1991)

Exposure

Also for this herbicide, diffuse input to surface waters is expected. The database lists 12 samples from rivers, nine from Lake Constance and six from effluents that were measured for



bifenox acid, there are no detects over the LOQ (3 to 100 ng/L). Recently, several river water samples (n=58) were analysed at the Eawag with an LOQ for bifenox acid of 5 ng/L. In these studies (Longrée and Singer, 2013; Longrée et al., 2013) the maximum concentration measured was 15 ng/L.

In the literature, information on bifenox (acid) is relatively scarce and analysis is hampered by LOQ problems (see also Loos, 2012). Recently, larger data sets were generated in Germany and France. In NRW, bifenox was not found above the LOQ of 25 to 50 ng/L in 399 samples from 63 rivers (NRW, 2013b). In Baden Württemberg, one detect at the LOQ of 50 ng/L occurred in 2'109 groundwater samples (Landesanstalt für Umwelt, 2011). In Figure 1, there are data for 61 LAWA monitoring stations. For 43 sites the LOQ was higher than the AA-EQS (grey bar) and at 18 sites either the LOQ or measured concentrations were below the AA-EQS (blue bar). In a large data set from France there were only few detects, but as elsewhere, LOQs were mostly higher than the AA-EQS (Table 1 of the Annex and Figure 2).

Risk

The data set for bifenox is too limited to determine possible risks of EQS exceedance and also a high LOQ hampers the interpretation of data (Figure 6). However, bifenox acid only slightly exceeded the AA-EQS in only three of 58 two-week composite samples while the MAC-EQS was not exceeded (Longrée and Singer, 2013; Longrée et al., 2013). Also when viewed in an international context, the risk of significant bifenox AA-EQS exceedance seems limited. For example, there were no exceedances for the 18 LAWA sites where appropriate LOQs were achieved (shown in Figure 1).

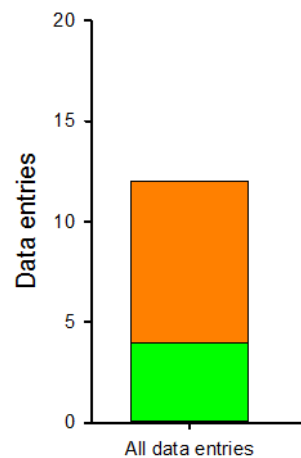


Figure 6: Distribution of bifenox data across five quality classes for the AA-EQS (Table 3).

Recommendation

Given the paucity of data, further monitoring is advisable. The LOQ needs to be lowered to allow for a more robust interpretation of future monitoring data. Alternatively, passive sampling may have potential for monitoring bifenox (Smedes et al., 2010).



2.4.7 Cybutryne (Irgarol)

AA-EQS = 2.5 ng/L

“...Cybutryne (= Irgarol) is an effective triazine herbicidal biocide (or algicide) mainly used as an antifouling agent in paints for boats and vessels...” (Loos, 2012)

Exposure

Cybutryne is a biocide that is no longer used in Switzerland, at least not in protection products for construction materials (Burkhardt and Dietschweiler, 2013). There are 7'141 measurements of cybutryne in the database with more than 50% from the Rhine at the Weil am Rhein sampling station (Table 1). Only a minority of measurements (<2%) are without LOQ which is typically between 5 and 10 ng/L. Lower LOQs are possible, e.g. for Lake Constance an LOQ of 0.1 ng/L was reported in the MicroPoll database. Loos (2012) reports that it should be straightforward to develop an adequate method to measure cybutryne in surface waters at <0.3 times the AA-EQS, i.e. < 0.75 ng/L (Longrée and Singer, 2013, report an LOQ of 1 ng/L).

The average cybutryne concentration detected in Switzerland was 20 ng/L which is close to a tenth of the concentration in effluents (i.e. allowing for a 10 fold dilution; 10 ng/L). Measurements made in Germany (Arle et al., 2014) give a slightly better picture: for 28 of 63 LAWA locations cybutryne was determined to be below the AA-EQS but above the LOQ (blue bar in Figure 1); cybutryne exceeded the AA-EQS at five locations (red bar in Figure 1). However, also for this data series Arle et al., 2014, LOQ was larger than the AA-EQS at 30 locations (grey bar in Figure 1). Information on cybutryne from France is limited (Figure 2) and Empodat contains 9% detects for just under 5'000 measurements. The average and 90th percentile concentrations in Empodat exceed the AA- and MAC-EQS values considerably (Annex Table 1).

Risk

The LOQ is too high to critically evaluate the data against the AA-EQS of 2.5 ng/L. Based on the evaluation scheme in Table 3 and the LOQ alone, almost all samples would be evaluated as “orange” at best (Figure 7). On the one hand, the measurements in Weil am Rhein, with 1% detects between 5 and 11 ng/L and an LOQ of 5 ng/L show that, at least in a large catchment, the concentrations are less than double the AA-EQS. On the other hand, measurements of 1.3 ng/L in Lake Constance are indicative of a possible widespread exposure at concentrations reaching 50% of the AA-EQS. The MAC-EQS is exceeded in 105 samples, this is 1.5% of all samples listed in the database. As the use of cybutryne in construction materials has stopped, the input into the environment and with it the risk of EQS exceedances will likely decline.

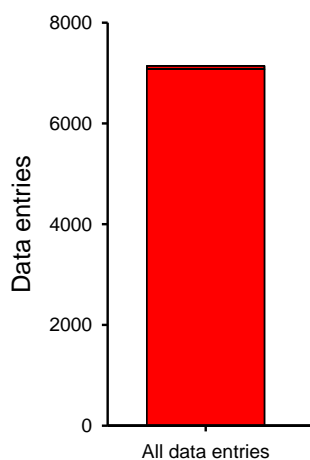


Figure 7: Distribution of cybutryne data across five quality classes for the AA-EQS (Table 3).



Recommendation

To critically evaluate the distribution of the environmental concentrations, measurements with lower LOQs are essential. Concentrations are expected to decline but additional monitoring, including harbours and effluent impacted rivers is advisable to affirm and quantify trends.

2.4.8 Cypermethrin

AA-EQS = 0.08 ng/L

“...Cypermethrin is a synthetic pyrethroid insecticide used to control pests, such as moth pests of cotton, fruit and vegetable crops, including structural pest control, landscape maintenance, for residential and garden use...” Marigoudar et al., 2009

Exposure

Cypermethrin is allowed for use on a variety of crops (BLW, 2014) and diffuse release to surface waters is expected (Jorgenson et al., 2013). Four out of 5'829 values in the database considerably exceed the LOQ and at the same time the AA- and MAC-EQS; they were 50, 61, 82 and 160 ng/L; three measurements are listed with a value just below the LOQ: 30, 40 and 46 ng/L. LOQs can be as low as 5 ng (for 90% of samples from Weil am Rhein, Table 2), but otherwise LOQs range between 10 to 50 ng/L and up to 100 ng/L. There are 53 measurements in waste water, but no detects at LOQs of 200 and 400 ng/L. In Germany, cypermethrin was not detected above LOQ at 47 LAWA monitoring stations (Figure 1). However, in the United Kingdom the use of cypermethrin in sheep dips can lead to very high concentrations (Moore and Waring, 2001 and Carr, 2013). This explains the many detects and high concentrations listed in Empodat (Annex Table 1), as in the case of cypermethrin, 77% of the Empodat data including all detects come from the UK.

In a review on analytical methods for priority substances, Loos (2012) reports the best LOQ for cypermethrin at 1 ng/L. As the target for the LOQ is ca. 20 pg/L (0.3 times the AA-EQS), it is obvious that past and current analytical methods are not sufficient to quantify cypermethrin at appropriate levels in the water phase. Although cypermethrin has been detected in several countries in the EU (Commission, 2010; e.g. 90 ng/L is reported for France), it is not possible to realistically characterise the exposure.

Risk

Although there are many database entries for this substance, the gap between the LOQ and the EQS values is extreme. When all measurements are treated as detects at the LOQ (e.g. Müller, 2011) or even detects at 50% of the LOQ (e.g. UBA, 2009), this would result in all data falling into the risk class “red” (i.e. aqueous concentrations > 10 times the AA-EQS, Table 3; Figure 8).

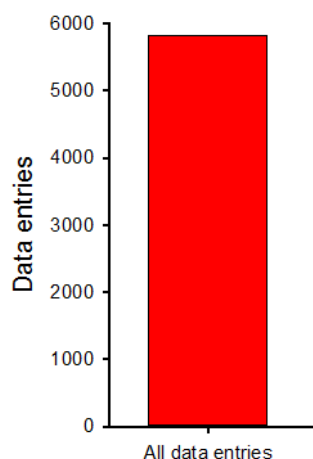


Figure 8: Distribution of cypermethrin data across five quality classes for the AA-EQS (Table 3).

Recommendation

It is clear that better methods are needed to monitor cypermethrin in the water phase. At the moment the only realistic option seems to be the use passive sampling following methods that have been used for dioxins and dl-PCBs. Such work is underway in the UK (Carr, 2013) and at the Eawag (Fässler and Stöckli, 2013). It appears that detection in the range of the AA-EQS (0.01 to 0.1 ng/L) is possible (Moschet et al., 2014) which would make the method suitable to monitor – with some uncertainty – for AA-EQS compliance. Finally, the Cantons have a working group to establish better analytical methods for pyrethroids (C. Balsinger, ZH).

2.4.9 Dichlorvos

AA-EQS = 0.6 ng/L

“...Dichlorvos is usually used as an agricultural insecticide on crops and stored products but is also used as an antihelminthic (worming agent)...” (Das, 2013)

Exposure

In Switzerland, dichlorvos is no longer allowed as an insecticide in agriculture (Baur and Baur, 2011; Bundesrat, 2013) and also residential use of dichlorvos will be restricted (BAG, 2014). In the database, with almost all data (96%) coming from the Rhine at the Weil am Rhein sampling station, only one of 3'999 sample entries has a measured value (21 ng/L). The LOQ is typically 5 ng/L and thus around 10-fold above the AA-EQS. A report on Swiss ground water (Kilchmann et al., 2009) lists measurements at 10 locations, with no detects above an LOQ of 5 ng/L. Again, this LOQ is high and besides, dichlorvos is prone to rapid degradation in water (Tomlin 1994 in Pan et al., 2012), it is typically not expected to be present in groundwater.

Dichlorvos is volatile and relatively high concentrations have been reported in the past in rain-water in The Netherlands (up to 95 ng/L; see Hamers et al., 2001). In recent surveys in The Netherlands, dichlorvos was not detected in the Rhine in 2011 or 2012; also for these surveys, the LOQs were much higher than the EQS (5 to 50 ng/L). For 86 German LAWA sites, sampled between 2005 and 2007, two detects (48 and 240 ng/L) were reported for 1702 measurements with LOQs ranging between 0.6 and 120 ng/L (Heidemeier et al., 2007). In a more recent review of LAWA data (2009-2010) acceptable LOQs were only available for nine of 107 sites, LOQs for the other sites were (still) too high (Figure 1). For recent data from France a similar picture



emerges: sufficiently low LOQs for ca. 10% of the samples; too high a LOQs for most samples, and; AA-EQS exceedances for ca. 0.5% of measurements.

Risk

In principle, a risk of AA-EQS exceedance cannot be determined on the basis of the available exposure data (Figure 9). However, given the fact that use of dichlorvos has been severely restricted and the fact that it is volatile and short lived in the water phase, the prospect for future exposure and EQS exceedance is very limited.

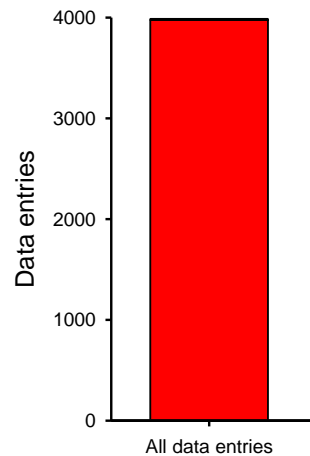


Figure 9: Distribution of dichlorvos data – one detect and all other data with a high LOQ – across five quality classes for the AA-EQS (Table 3).

Recommendation

Loos (2012) suggests that that a sensitive chemical analyses for dichlorvos will be extremely hard to accomplish, however, data from Germany and France indicates LOQs below the AA-EQS can be achieved (Figure 2). Although recent data from France indicates risk of EQS exceedance (i.e. in 0.5% of samples), given the low risk probability additional monitoring is not required.

2.4.10 Hexabromocyclododecan AA-EQS = 1.6 ng/L

“...Hexabromocyclododecan is a flame retardant mainly added to polystyrene foam used as thermal insulation in the construction industry, and to textiles, upholstery, packaging material, and electric and electronic equipment...” (Miège et al., 2012)

Exposure

Hexabromocyclododecan (HBCD) was banned in 2013 with a five-year phase out for some use categories (extruded and expanded polystyrene used in the insulation of buildings; BAFU, 2013a). HBCD is not listed in the MicroPoll database. It is currently not possible to detect HBCD in the water phase at 30% of the level of the AA-EQS (Loos, 2012). HBCD is persistent and as it is hydrophobic, HBCD strongly binds to sediment Covaci et al., 2006. There is no information on HBCD for LAWA sites (Figure 1; Arle et al., 2014).



Regarding HBCB concentrations in biota, Gerecke et al. (2008) reviewed data on fish. In brown trout, caught in waste water impacted rivers, HBCD ranged between 44-250 ng/g lipid weight (see Vermeirssen et al., 2005, for details on sampling locations). When a 3% lipid content is assumed for brown trout (Schmid et al., 2010; Kaya and Erdem, 2009), the HBCD biota concentration range transforms to 1'500 to 8'300 ng/kg wet weight. Although it has to be noted that these are results of a few limited sampling campaigns – and results date back some 10 years – the observations are substantiated by data from the German Environmental Specimen Bank. These show that the biota-EQS is not exceeded (Schudoma and Schröter-Kermani, 2013). However, data from fish collected in the Rhone in France indicate that the biota-EQS can be reached. The maximum alpha-HBCD concentration was reported at 766 ng/g dry weight (Miège et al., 2012). This value can be transformed to an approximate 176'000 ng/kg wet weight which is just above the biota-EQS of 167'000 ng/kg wet weight (see Table 2).

Risk

As there is no information on concentrations in the water phase, a risk of EQS exceedance cannot be determined. For biota the risk appears to be low. In 2003, HBCD concentrations in Swiss brown trout were 20 to 115 fold below the biota-EQS (Gerecke et al., 2008). There may be a significant HBCD exposure risk to fish eating birds (e.g. herons), however. In a review by Covaci and others (2006) it was shown that birds tend to show a much higher level of exposure than fish. As the substance is banned the exposure will likely decrease but due to its persistency and hydrophobicity, contaminated sediments will continue to serve as a source of HBCD.

Recommendation

As with other hydrophobic compounds in the set of priority substances, passive sampling may be an (the only) option as a monitoring tool to: 1) sample the water phase; and, 2) serve as a surrogate for biota monitoring (ICES, 2013; Allan et al., 2011). Given the extremely low AA-EQS value even the possibilities of passive sampling may be limited. The method should be explored, however, to attempt and fill the gap on aqueous concentrations. In addition, sediment sampling can be considered in the context of hydrophobic compounds.

2.4.11 Heptachlor and Heptachlorepoxyde AA-EQS = 0.0002 ng/L

“...Heptachlor is an insecticide which acts through contact or ingestion. It has been used primarily to control soil insects and termites, but also to combat malarial mosquitoes and crop pests...”
(BAFU, 2004)

Exposure

This compound has been banned since the mid-eighties. There are no detects in the database for 119 measurements, all from the Rhine at Weil am Rhein with an LOQ of 2 ng/L. In Germany (2005-2007; Heidemeier et al., 2007), two heptachlor detects were reported (10 and 15 ng/L) for 1'927 measurements with an LOQ range of 0.1 to 50 ng/L. For more recent German data (2009-2011), AA-EQS exceedance has been reported for heptachlorepoxyde at two of 40 LAWA sites. For other LAWA locations, LOQs were too high to determine EQS compliance (Figure 1), a situation that mirrors that of France (Figure 2). These observations support the conclusion that current possibilities of chemical analyses are insufficient for compliance monitoring in water (Loos, 2012).

Also for biota monitoring data reported from Europe, LOQs are too high for compliance monitoring purposes. For Austria an LOQ is reported of 500 ng/kg, 75-fold above the biota-EQS of 6.7



ng/kg fresh weight (Uhl et al., 2010). Fish sampled from the Elbe in Germany in 2009 did not exceed the LOQ of 100 ng/kg (2010), which is 15-fold above the biota-EQS. Finally, analyses of samples from the German Environmental Specimen Bank show that the LOQs were well above the biota-EQS (Schudoma and Schröter-Kermani, 2013).

Risk

As there are no data, a risk cannot be determined.

Recommendation

Analogous to the situation for e.g. PCBs, passive sampling may be possible to determine a risk for EQS exceedance in both the water phase as well as biota (ICES, 2013). However, the extremely low heptachlor EQS values are likely to go beyond even the possibilities of passive sampling.

2.4.12 Terbutryn

AA-EQS = 65 ng/L

“...Terbutryn is a biocide and as Irgarol® 1051 it is used in paints for facades or ship hulls. It is also used as a control agent for grasses and weeds which might also lead to a washing-off into surface waters...” (Richard, 2012)

Exposure

Terbutryn is used as a biocide in protection products for construction materials, for example, in facades. Its input into the aquatic environment is both diffuse and via point sources. Terbutryn is the compound for which most information is available in the MicroPoll database (n=12654; Table 2), with half of the data coming from the Weil am Rhein sampling station. The compound was detected in 11% of all samples with an average of 21 ng/L. Based on a 10-fold dilution of treated sewage effluent, the expected surface water concentration would be 35 ng/L. LOQs are typically between 5 to 10 ng/L. This is satisfactory with respect to the level of the AA-EQS (i.e. 65 ng/L). The highest terbutryn value in the database is 2393 ng/L, seven-fold the AA-EQS.

In The Netherlands, terbutryn is not detected above 10 ng/L in the main freshwater courses (RIWA, 2011 and 2012). Along the Rhine in Germany, terbutryn concentrations are typically around 4 ng/L (years 2008-2011 for station Lauterbourg; (IKSR, 2011b). Other data from Germany, but also from France and Empodat, provide a similar picture: no problems with LOQs and some EQS exceedances (<10%; Figure 2).

Risk

There are 73 measurements that are above the AA-EQS, this comprises only a fraction of the data: 0.6% (Figure 10). Significant exceedances of the EQS occur mainly in smaller rivers (Figure 11; compare data from the Rhine with those from the remaining sampling stations). The MAC-EQS was exceeded in six samples in smaller rivers (i.e. excluding the data from Weil am Rhein, Table 1) or 0.1% of measurements. It can be concluded that the risk of EQS exceedance is low.

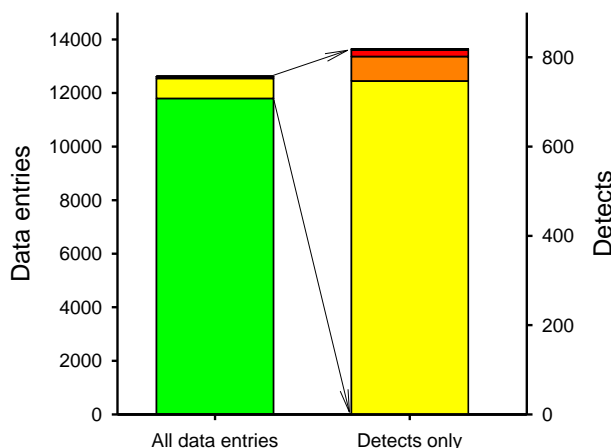


Figure 10: Distribution of terbutryn data across five quality classes for the AA-EQS (Table 3). Left bar, evaluation of all data entries in the MicroPoll database; right bar, distribution of the quality classes for the detects.

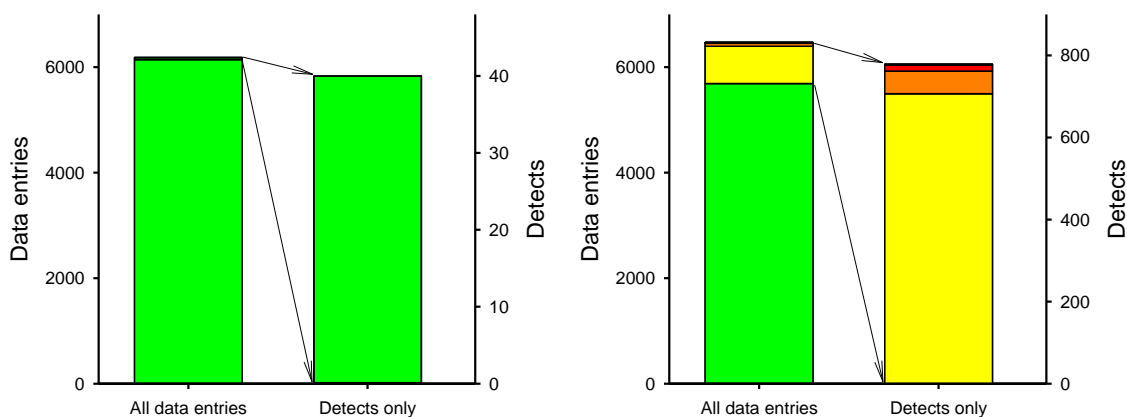


Figure 11: Distribution of terbutryn data across five quality classes for the AA-EQS (Table 3). Left panel, data from the Rhine station “Weil am Rhein” only; right panel, data from the remaining monitoring stations. Left bars, evaluation of all data entries; right bars, distribution of the quality classes for the detects.

Recommendation

There are sufficient monitoring data and no gaps with respect to either data or analysis methods. Unless there are indications of increased use of the biocide or concerns about small catchments that may be at risk, no additional monitoring or method development for terbutryn is required.



2.4.13 Irbesartan

AA-EQS = 704'000 ng/L

"...Irbesartan is an angiotensin II receptor antagonist used in the treatment of hypertension. It may also delay progression of diabetic nephropathy and is also indicated for the reduction of renal disease progression in patients with type 2 diabetes..." (Lakshmi et al., 2012)

Exposure

Irbesartan is a pharmaceutical and thus released via treated sewage effluents, however, the database does not contain data on irbesartan in waste water. A study by Eawag put the concentration in effluent between 1'000 to 3'000 ng/L (Götz et al., 2010b). This is in line with measurements done in effluent in Germany (1'730 ng/L; Bayer et al., 2013), but slightly above an average concentration of 480 ng/L (median: 85 ng/L) reported for a survey of 90 European waste water treatment plants, including five from Switzerland (Loos et al., 2013).

For river water, all irbesartan data in the database are from the Rhône; 110 of 145 entries comprise 2 week composite samples of the discharge of the Rhône into Lake Geneva (Porte du Scex). Irbesartan in the Rhone occurred in large discharge peaks, particularly in 2007 and 2008. Similar high discharges were also observed for carbamazepine (Bernard et al., 2012). As for carbamazepine, the load of irbesartan in the Rhône has decreased considerably over the years, from a high of 262 kg in 2008 to 32 kg in 2011 (Bernard et al., 2012). The situation in the Rhône may represent a special exposure scenario (i.e. industrial discharges).

The average concentration for detects in the Rhône is 41 ng/L, although this value is likely not representative for other catchments in Switzerland and for the current situations in the Rhône. Longrée and Singer (2013) measured irbesartan in the Rhône in three two-week composite samples and found only low concentrations, between 3.7 and 13 ng/L, which were similar to concentrations of diclofenac that were measured in the same samples. Diclofenac and irbesartan have fairly similar concentrations in effluent, so similar concentrations in the same river water sample are plausible. Data from Germany indicate that concentrations of up to 340 ng/L in surface water are possible, these higher values are also similar to what is expected on the basis of a 10-fold dilution of treated effluent (Bayer et al., 2013).

Risk and recommendations

As the AA-EQS for irbesartan is very high and the measured or expected aqueous concentrations are lower by a factor of at least 1'000, there is no risk of EQS exceedance and further monitoring for this compounds is not necessary to refine the risk of EQS exceedance (Figure 12). There are, however, analytical issues with the measurements of this compound (as well as for valsartan), and measured river water concentrations are often lower than expected based on concentrations found in effluents (Heinz Singer Eawag, personal communication). Given the big gap between the EQS and measured concentrations, these analytical uncertainties have no impact on the risk assessment.

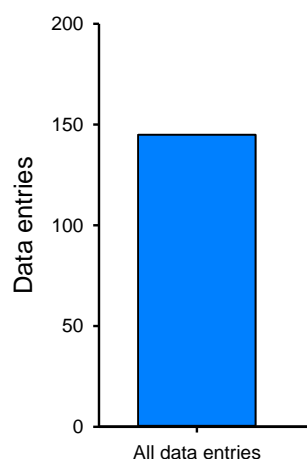


Figure 12: Distribution of irbesartan data across five quality classes for the AA-EQS (Table 3).

2.4.14 Valsartan

AA-EQS = 560'000 ng/L

"...Valsartan is an antihypertensive agent and is used as angiotensin-II antagonist..."
(Thanusha et al., 2010)

Exposure

As for irbesartan, valsartan is mainly released to the aquatic environment via treated sewage effluents. For valsartan only six effluent data are available from the database, with a maximum concentration of 4200 ng/L. Similarly high concentrations of up to 5750 ng/L were found in a German study (Bayer et al., 2013). As for irbesartan, the distribution of the river water data in the MicroPoll database is very regional. Forty-six of 70 entries are from the Weil am Rhein monitoring station and the average concentration in river water is 35 ng/L; with only one measurement below the LOQ (5 ng/L). This concentration is very similar to the median concentration provided in a recent study by Mathias Ruff et al. (ca. 30 ng/L; Ruff et al., 2013). Measured valsartan concentrations in several German rivers range up to 440 ng/L (Bayer et al., 2013).

Risk and recommendations

As for irbesartan, measured concentrations are lower than the AA-EQS by a factor of around 1'000 (Figure 13). There is no risk of EQS exceedance and further monitoring for this compounds is not necessary to refine this risk.

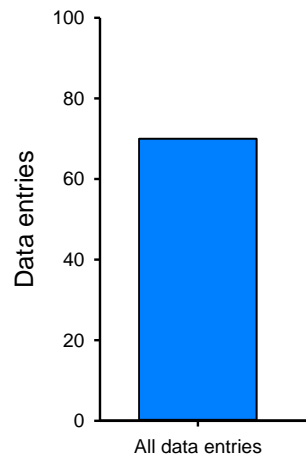


Figure 13: Distribution of valsartan data across five quality classes for the AA-EQS (Table 3).

2.4.15 Ciprofloxacin

AA-EQS = 89 ng/L

“...Ciprofloxacin is an antibiotic used to treat certain infections caused by a wide spectrum of bacteria...” Mokhtarani et al., 2008

Exposure

Ciprofloxacin is used both in human and in veterinary medicine. Thus emissions to the aqueous environment occur via both point and diffuse sources. In the database, the average ciprofloxacin concentration is 34 ng/L and the highest 53 ng/L; half of the data come from the Weil am Rhein monitoring station. Only a quarter of the entries are provided with an LOQ (20 ng/L). The average of the MicroPoll data (34 ng/L) is very close to that of the Empodat data (39 ng/L). After 10-fold dilution, the average concentration measured in treated effluent in Switzerland is close to the average found in river water (29 ng/L compared to 34 ng/L; Table 2). The average concentration in effluents (294 ng/L) is similar to values reported from Austria (250-350 ng/L; Clara et al., 2010). These concentrations are also in line with observations made in treated sewage effluents and the river Glatt (ZH; Giger et al., 2003). However, in a study on 90 European treated effluents (Loos et al., 2013), the average ciprofloxacin concentration was 96 ng/L, which is three fold below the level given in Table 2 (i.e. 294 ng/L).

The LOQ in the database of 20 ng/L is sufficiently low (more than three-fold below the EQS), but it would be beneficial to have a lower LOQ and this seems possible. For example, Tuc Dinh et al. (2011) report an LOQ of 3.3 ng/L, De la Cruz et al. (2013) report 2 ng/L and Zimmermann-Steffens et al. (2013) report an LOQ below 1 ng/L.

Risk

Compared to the previous two pharmaceuticals (and also metformin), the EQS of ciprofloxacin is relatively low (89 ng/L) and detected concentrations in river water are not far below the AA-EQS. The number of data is low, but neither the AA-EQS nor MAC-EQS were exceeded (Figure 14). Although the input via treated sewage effluent and its associated risk can be assessed, there may be risks associated with runoff from agricultural fields.

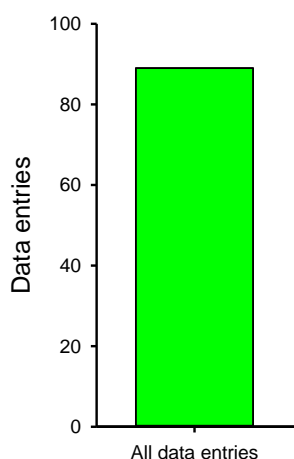


Figure 14: Distribution of ciprofloxacin data across five quality classes for the AA-EQS (Table 3).

Recommendation

The evaluation of risk would benefit from a lower LOQ and more monitoring data. Currently the data are regional, a broader overview is desirable. Information is also needed about what happens during rain events, where runoff from agricultural sites (animals treated with ciprofloxacin) may affect smaller streams. Information on the use pattern of ciprofloxacin in agriculture would also be beneficial.

2.4.16 Propranolol

AA-EQS = 160 ng/L

“...Propranolol is a beta-adrenergic blocking drug widely prescribed for the treatment of cardiac arrhythmia, sinus tachycardia, angina pectoris and hypertension...” (Fernández-Sánchez et al., 2003)

Exposure

About 15% of entries in the database show a detection above the LOQ which was approximately 10 ng/L. The average value measured was 18 ng/L and the average effluent concentration divided by 10 comes to 9 ng/L. Also a study for the Glatt catchment indicates measured and modelled concentrations that range up to 20 ng/L (Alder et al., 2010). For a catchment in the UK, 90th percentile values up to 50 ng/L were modelled (Johnson et al., 2007). River water and effluent concentration data in Empodat are in line with data from Switzerland.

Risk

All data in the database are below the AA-EQS (Figure 15). Given the release pattern that is associated with a fairly constant use of pharmaceuticals by the population (Ort et al., 2009), both the water concentrations and effluent concentrations indicate that the probability of AA-EQS exceedance is low. Even the average (undiluted) effluent concentration typically reaches only half the AA-EQS and a risk of MAC-EQS exceedance is highly improbable.

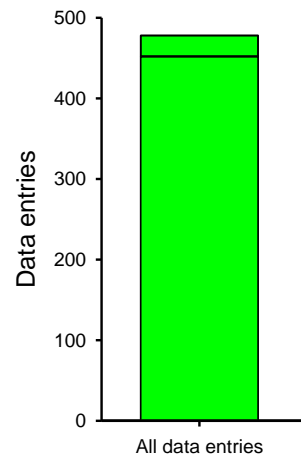


Figure 15: Distribution of propranolol data across five quality classes for the AA-EQS (Table 3).

Recommendation

As the main risk to the environment comes from well-defined point sources, i.e. effluents, more monitoring data would be helpful to further characterise the risk and allow for a more robust risk evaluation, particularly for effluents that carry hospital waste water.

2.4.17 Metformin

AA-EQS = 1'000'000 ng/L

"...Metformin is a widely used anti-diabetic agent for the treatment of type 2 diabetes..." (Klein et al., 2004)

Exposure

Data in the MicroPoll database on metformin mainly originate from canton Bern (84% of the data) and the Weil am Rhein monitoring station (15% of the data). The average for detects is 362 ng/L which is well below the EQS (the risk quotient, RQ = aqueous concentration divided by the EQS, is below 0.001). Also the data from treated effluent (average concentration ca. 10 µg/L) do not indicate a possible risk for surface waters. Multiple samplings along five major rivers in Germany showed an average concentration of 550 ng/L (Scheurer et al., 2009). This average is very close to the values reported for a large sampling campaign in the catchment of the Maas (The Netherlands), namely 0.6 µg/L Houtman et al. (2013), and the median concentration listed in Empodat (545 ng/L, Annex Table 1).

Risk and recommendation

As for both sartans (i.e. valsartan and irbesartan), the effluent and river water concentrations are much lower than the AA-EQS and the MAC-EQS (Figure 16). Therefore, there is no plausible risk of EQS exceedance and additional monitoring for this compound, to refine a risk assessment, is not required.

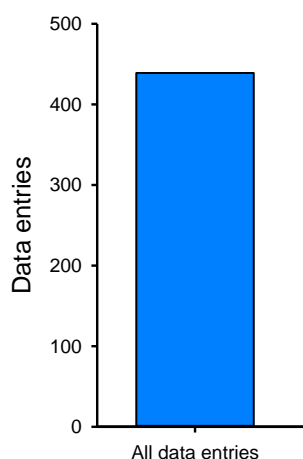


Figure 16: Distribution of propranolol data across five quality classes for the AA-EQS (Table 3).

2.5 Overall summary of exposure and risk evaluation

Table 4 summarises the degree of exposure and risk of EQS exceedance that have been elaborated in sections 2.4.1 to 2.4.17. As the MicroPoll database is very heterogeneous and does not contain enough data for all compounds, conclusions or recommendations summarised in Table 4 are based on information from Switzerland as well as surrounding countries. This is justified as both Tables 2 and Annex Table 1 as well as Figure 2 indicate that – when exposure data exists – the exposure situation in Switzerland is not that different from the exposure situation in surrounding countries.

Table 4: Summary of exposure and risk evaluation. Blue shading indicates a lack of critical information for a substance (e.g. dicofol) and a specific parameter (e.g. entries MicroPoll database).

No.	Name of substance		Database entries MicroPoll database	Other Swiss data for water phase	Swiss biota data	Water LOQ>AA-EQS MicroPoll database	Water LOQ>AA-EQS Germany ^b	Biota LOQ>EQS (Switzerland and Germany)	AA-EQS exceedance MicroPoll database	MAC-EQS-exceedance MicroPoll database	Biota-EQS exceedance	Qualification of exposure and risk relevance
34	Dicofol	Banned	no	no ^a	no ^a	-	yes	yes	unknown/unlikely	-	unknown	low
35	PFOS	Phasing out (diffuse inputs)	few	yes	no ^a	yes	yes	yes	likely	no	likely	high
36	Quinoxifen	In use	no	no ^a	-	-	no	-	unknown/unlikely	unknown/unlikely	-	unknown
37	Dioxins/dl-PCBs	Banned (diffuse inputs)	-	-	yes	-	-	no	-	-	yes	high
38	Acionifen	In use	few	no	-	no	no	-	unlikely	yes ^c	-	unknown
39	Bifenox (acid)	In use	few	yes	-	yes	yes ^h	-	unlikely	unknown	-	unknown
40	Cybutryne (Irgarol)	In use	many	yes	-	yes	yes ⁱ	-	likely	yes ^d	-	high
41	Cypermethrin	In use	many	yes ^a	-	yes	yes	-	unknown	yes ^e	-	unknown
42	Dichlorvos	Banned	many	no ^a	-	yes	yes ⁱ	-	unknown	yes ^f	-	low
43	Hexabromcyclododecan	Banned (diffuse inputs)	no	no ^a	yes	-	yes	no	unknown	unknown	no	unknown
44	Heptachlor epoxide	Banned (diffuse inputs)	few	no ^a	no ^a	yes	yes	yes	unknown	-	unknown	unknown
45	Terbutryn	In use	many	yes	-	no	no	-	unlikely	yes ^g	-	medium
	Irbesartan	In use	many	yes	-	no	-	no	no	no	-	no risk
	Valsartan	In use	few	yes	-	no	-	no	no	no	-	no risk
	Ciprofloxacin	In use	few	yes	-	no	-	no	no	no	-	low
	Propranolol	In use	many	yes	-	no	-	no	no	no	-	low
	Metformin	In use	many	yes	-	no	-	no	no	no	-	no risk

a passive sampling data

b see Figure 1 and Arle et al. 2014; reflects % of LAWA sites where LOQ>EQS

* no data were found

- not applicable

For

h 70% LAWA sites

i 63% LAWA sites

j 92% LAWA sites

Qualification of the "yes" evaluation

c few data (183 measurements)

d 105 of 7144 measurements

e 7 of 5829 measurements but LOQ above MAC-EQS

f 1 of 3999 measurements but LOQ above MAC-EQS

g 6 of 12654 measurements



No.	Name of substance		Database entries MicroPoll database	Other Swiss data for water phase	Swiss biota data	Water LOQ>AA-EQS MicroPoll database	Water LOQ>AA-EQS Germany ^b	Biota LOQ>EQS (Switzerland and Germany)	AA-EQS exceedance MicroPoll database	MAC-EQS- exceedance MicroPoll database	Biota-EQS exceedance	Qualification of exposure and risk relevance
34	Dicofol	Banned	no	no ^a	no ^a	-	yes	yes	unknown/unlikely	-	unknown	low
35	PFOS	Phasing out (diffuse inputs)	few	yes	no ^a	yes	yes	yes	likely	-	likely	high
36	Quinoxifen	In use	no	no ^a	-	-	no	-	unknown/unlikely	unknown/unlikely	-	unknown
37	Dioxins/dl-PCBs	Banned (diffuse inputs)	-	-	yes	-	-	no	-	-	yes	high
38	Aclonifen	In use	few	no ^a	-	no	no	-	unlikely	yes ^c	-	unknown
39	Bifenox (acid)	In use	few	yes	-	yes	yes ^h	-	unlikely	unknown	-	unknown
40	Cybutryne (Irgarol)	In use	many	yes	-	yes	yes ⁱ	-	likely	yes ^d	-	high
41	Cypermethrin	In use	many	yes ^h	-	yes	yes	-	unknown	yes ^e	-	unknown
42	Dichlorvos	Banned	many	no ^a	-	yes	yes ⁱ	-	unknown	yes ^f	-	low
43	Hexabromcyclododecan	Banned (diffuse inputs)	no	no ^a	yes	-	yes	no	unknown	unknown	no	unknown
44	Heptachlor epoxide	Banned (diffuse inputs)	few	no ^a	no ^a	yes	yes	yes	unknown	-	unknown	unknown
45	Terbutryn	In use	many	yes	-	no	no	-	unlikely	yes ^g	-	medium
	Irbesartan	In use	many	yes	-	no	-	no	no	no	-	no
	Valsartan	In use	few	yes	-	no	-	no	no	no	-	no
	Ciprofloxacin	In use	few	yes	-	no	-	no	no	no	-	low
	Propranolol	In use	many	yes	-	no	-	no	no	no	-	low
	Metformin	In use	many	yes	-	no	-	no	no	no	-	no

a passive sampling data

b see Figure 1 and Arle et al. 2014; reflects % of LAWA sites where LOQ>EQS

* no data were found

- not applicable

For

h 70% LAWA sites

i 63% LAWA sites

j 92% LAWA sites

Qualification of the "yes" evaluation

c few data (183 measurements)

d 105 of 7144 measurements

e 7 of 5829 measurements but LOQ above MAC

f 1 of 3999 measurements but LOQ above MAC

g 6 of 12654 measurements

Table 5 summarises the results in a approach taken from risk assessment. The first column lists the risk quotient (RQ) as the 90th percentile of monitoring data divided by the AA-EQS. Except for the five pharmaceuticals at the bottom of the table, most compounds lack sufficient monitoring data to provide the RQ. Also the second column (detection frequency, DF) is hampered by lack of data. Therefore, a risk probability (i.e. RQ x DF) can only be provided for two of 12 EU EQS substances and for the five Swiss relevant pharmaceuticals.

Table 5: Risk probabilities and monitoring recommendations for 12 EU EQS substances and five Swiss relevant pharmaceuticals.

No.	Name of substance	Risk quotient = 90th percentile River water exposure / AA-EQS	Detection frequency river water (DF) [%]	Risk probability = RQ x DF [%]	Recommendation
34	Dicofol	no monitoring data	no monitoring data	unknown	improve monitoring
35	PFOS	LOQ insufficient	(27.6)	on biota relevance	analytical improvement
36	Quinoxifen	no monitoring data	no monitoring data	unknown	improve monitoring
37	Dioxins/dl-PCBs	-	no monitoring data	unknown	improve monitoring
38	Aclonifen	4.0	10.4	(41.6)	(risk reduction)
39	Bifenox (acid)	no monitoring data	no monitoring data	unknown	improve monitoring
40	Cybutryne (Irgarol)	LOQ insufficient	(3.9)	unknown	analytical improvement
41	Cypermethrin	LOQ insufficient	(0.12)	unknown	analytical improvement
42	Dichlorvos	no monitoring data	no monitoring data	unknown	analytical improvement
43	Hexabromcyclododecan	no monitoring data	no monitoring data	unknown	unclear
44	Heptachlor epoxide	no monitoring data	no monitoring data	unknown	unclear
45	Terbutryn	0.6	11	6.6	risk reduction
	Irbesartan	0.000108	64.1	0.007	no need for action
	Valsartan	0.000102	98.6	0.010	no need for action
	Ciprofloxacin	0.596	7.5	4.470	no need for action
	Propranolol	0.344	13.8	4.747	no need for action
	Metformin	0.00054	76.3	0.041	no need for action



2.6 Conclusions

The 17 compounds constitute a very diverse group – each compound has its specific issues with respect to either the quantity and quality of exposure data, risk of EQS exceedance and requirements for further monitoring. Even given this diversity, several distinct patterns emerge.

- Six of the 12 new EU-EQS substances are banned or are being phased out. Except for dicofol and dichlorvos, these compounds (PFOS, dioxins and dl-PCBs, HBCD, heptachlor) still remain of concern, as they have a long life span in the environment, particularly in sediments, and continue to be emitted to the aquatic environment from landfills.
- About half the compounds suffer from inadequate chemical detection methods. Although this aspect may soon be ameliorated for PFOS (detection is only an issue with reference to the low EU AA-EQS) and cybutryne, the compounds HBCD, heptachlor and cypermethrin have such low EQS values that current technology does not allow for appropriate compliance monitoring.
- For a number of compounds, risks of EQS exceedance are evident: dl-PCBs (biota-EQS exceedance), PFOS (EU AA-EQS and biota-EQS exceedance), cybutryne (AA- and MAC-EQS exceedance)
- For some compounds, the available data do not allow an assessment of the risk of EQS exceedance: HBCD (water data missing), heptachlor (water and biota data missing), cypermethrin (water data missing), PFOS (lacking biota data)
- For three of five pharmaceuticals (irbesartan, valsartan and metformin), environmental concentrations are much lower than EQS values. Although often only few and regionally limited data are available, there is no concern at the give EQS (even when considering the undiluted effluent concentrations of the three pharmaceuticals).
- A small group of compounds is of low priority, for various reasons. For terbutryn many data are available and risks of EQS exceedance are limited, except perhaps in small catchments. Dicofol has long been banned and has a short half-life in water. Dichlorvos is banned and degrades rapidly. For ciprofloxacin and propranolol use patterns and environmental fate model suggest a low risk of EQS exceedance.
- Additional monitoring is recommended for a number of compounds. These are: quinoxifen, aclonifen, bifenoX and ciprofloxacin. To some degree this also concerns PFOS (when considering the low EU AA-EQS value), where additional monitoring would help to affirm an apparent downward trend in concentrations.
- The MicroPoll database contains information on effluent and river water concentrations. When average effluent concentrations are divided by 10 (i.e. representing a 10-fold dilution of effluent in river water) the resulting concentrations are often between 2-fold above or 2-fold below the average concentrations in rivers. This appears a reasonable approach, but may not apply for small catchments or during periods of drought and the approach will not work for compounds largely entering the environment via diffuse input.
- For several compounds, passive sampling could be a useful monitoring tool. The method is already applied in Switzerland for PCBs and cypermethrin, although linking passive sampler data to aqueous concentrations or biota concentrations is still challenging. Other compounds that suit a passive sampling approach are dicofol, HBCD and heptachlor.



3 References

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4 Glossary

AA-EQS	annual average EQS
ARW	Arbeitsgemeinschaft Rhein-Wasserwerke – Association of Rhine water works
BAFU	Bundesamt für Umwelt (FOEN)
CAS	
CEP	Expert Prioritisation Committee
CMR	carcinogenic, mutagenic and reprotoxic
DDT	dichlorodiphenyltrichloroethane
DF	detection frequency
dl-PCB	dioxin-like PCB
EC	environmental concentration
EQS	environmental quality standard
EU	European Union
FOEN	Federal Office of the Environment (BAFU)
HBCD	hexabromocyclododecane
ICPR	International Commission for the Protection of the Rhine
IPChem	Integrated Platform for Chemical Monitoring
JRC	Joint Research Centre
LAWA	Länderarbeitsgemeinschaft Wasser – German working group on water issues of the Federal States and the Federal Government
LOQ	limit of quantification
MAC-EQS	maximum allowable concentration EQS
NRW	Nordrhein-Westfalen – North Rhine Westphalia
PBT	persistent, bioaccumulative and toxic
PCB	polychlorinated biphenyl
PFOS	perfluorooctane sulfonate
RBSPs	river basin specific pollutants
RIWA	Vereniging van Rijnwaterbedrijven – Association of Rhine water companies
RQ	risk quotient
RÜS	Rheinüberwachungsstation – Rhine monitoring station
TCDD	tetrachlorodibenzo-p-dioxin
TEQ	toxic equivalents
UBA	Umwelt Bundesamt
WFD	Water Framework Directive
WWTP	waste water treatment plant



5 Indices

5.1 List of Figures

Figure 1: The number of LAWA (Länderarbeitsgemeinschaft Wasser) monitoring stations for which the annual average concentrations for the period 2009-2011 was either below (blue) or above the AA-EQS (red) of 10 new EU priority substances. When the LOQ exceeded the AA-EQS, the data are labelled in grey (adapted from Figure 48 in Arle et al., 2014).	5
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Appendix 1 NORMAN Empodat data

Table 1. Summary of data extracted from the NORMAN Empodat database and from French monitoring campaigns (2007-2010).

No. ^a	Name of substance	AA-EQS (ng/L)	MAC-EQS (ng/L)	Bate-EQS (ng/kg)	LOQ range (ng/L)	Empodat River water # Detects / # Measurements	Switzerland River water # Detects / # Measurements	France LOQ range (ng/L)	France River water # Detects / # Measurements	River water average concentration (ng/L)	River water 90% concentration (ng/L)	WWTP ^b effluent # Detects / # Measurements	WWTP effluent average concentration (ng/L)	WWTP effluent 90% concentration (ng/L)
34	Dicofol	1.3	n/a	33000	5 - 40	12 / 3108	0 / 0	5 - 100	246 / 52469	14	44	no entries	-	-
35	PFOS	0.65	36000	9100	1 - 7	137 / 159	27 / 98	* - 200	11 / 119	10	20	no entries	-	-
36	Quinoxilylen	150	2700		10 - 65	1 / 2855	0 / 0	10 - 100	14 / 48836	10	10	no entries	-	-
37	Dioxins		n/a	6.5	-	no entries	no entries	0.1 pg/L	1363 entries	-	-	no entries	-	-
38	Aclonifen	120	120		45 - 100	5 / 800	19 / 183	10 - 100	644 / 59151	232	600	no entries	-	-
39	Bifenox (acid)	12	40		10 - 50	9 / 7350	0 / 12	10 - 100	19 / 54354	59	320	no entries	-	-
40	Cybutryne (Irgarol)	2.5	16		3 - 5	420 / 4725	277 / 7144	1	16 / 21	193	119	4 / 43	20	28
41	Cypermethrin	0.08	0.6		2 - 50	261 / 632	7 / 5829	4 - 300	19 / 41383	95	10	no entries	-	-
42	Dichlorvos	0.6	0.7		15 - 150	90 / 4104	1 / 3999	0.3 - 100	340 / 59965	113	158	no entries	-	-
43	Hexabromcyclododecan	1.6	500	167000	-	no entries	no entries	-	no entries	-	-	no entries	-	-
44	Heptachlor	0.0002	0.3	6.7	1 - 6	26 / 13948	0 / 119	5 - 100	94 / 31024	10	22	no entries	-	-
44	Heptachlorepoxyde	0.0002	0.3	6.7	1 - 6	7 / 12411	0 / 119	-	no entries	2	5	no entries	-	-
45	Terbutryn	65	340		10 - 50	1130 / 13055	1386 / 12654	1 - 250	893 / 57494	40	70	16 / 43	38	70
	Irbesartan	704000	19100000		-	no entries	93 / 145	-	-	-	-	no entries	-	-
	Valsartan	560000	9000000		-	no entries	69 / 70	-	-	-	-	no entries	-	-
	Ciprofloxacin	89	363		2 - 33	4 / 88	6 / 80	-	-	39	109	2 / 4	205	309
	Propranolol	160	12000		0.6 - 13	38 / 83	66 / 478	-	-	11	23	30 / 44	79	157
	Metformin	1000000	9100000		-	6 / 6	336 / 439	-	-	-	-	no entries	-	-

^a only summary data can be retrieved, max 680 ng/L median 545 ng/L
LOQ range is not fully inclusive - it is difficult to scan Empodat for these numbers

a EU EQS priority substance number
b waste water treatment plant