

Improving protection against chemical risks to European inland waters

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Executive Summary

EU and international policy have been tackling water and environmental pollution for nearly 50 years. Gross chemical pollution, exemplified by "dead rivers", has been successfully addressed in many cases. However, in its recent report, "European waters — Assessment of status and pressures 2018", based on data from Member States on the implementation of the Water Framework Directive (WFD), the European Environment Agency (EEA) found that despite action to reduce chemical pollution over many years, only 38 % of EU surface water bodies are in good chemical status. 46 % are not achieving this status, and 16 % are in unknown chemical status (EEA, 2018a).

The risk presented by hazardous substances is assessed under the WFD by comparing concentrations in the environment with environmental quality standards (EQS) for single substances. Some of the substances show high toxicity directly to organisms in the water, while others accumulate up the food chain and may therefore harm predators, which includes humans eating fish. This single substance approach has been used for many years, and fits well with regulation which seeks to control chemicals at source.

However, our understanding of the complex interactions between chemicals and living organisms has greatly increased over the last 20 years. At concentrations lower than those which kill directly, harmful chemicals may exert more subtle effects on organisms, for example limiting their ability to reproduce. Concern has been raised in relation to "the cocktail effect", referring to mixtures of substances which may be present at low concentrations and which may combine in complicated ways to affect health. Achieving good status in surface waters may therefore require a better understanding of the subtler links between ecological and chemical status. Some approaches to improving this understanding are described in chapter 2.

Improving protection against chemical risks means we need to know what the risks are. Returning to what monitoring and reporting currently provide, chapter 3 gives more specific information on the chemicals recently reported as causing failure under the WFD. It describes fate, status and pollution, and provides examples of measures for the 15 substances most commonly causing failure across Europe under the WFD, and a further 15 identified at Member State level as River Basin Specific Pollutants.

Among these substances, those described as "ubiquitous" cause the most failures. They are persistent and toxic substances, distributed worldwide, in many cases over many years. Mercury is the major cause of failure: nowadays in Europe its main sources from human activities are from coal burning for power generation and the chemical industry, while substantial amounts are also released from urban waste water treatment plants (EEA, 2018b). Brominated diphenylethers (pBDEs), which were used as flame-retardants, and polycyclic aromatic hydrocarbons (PAHs) which arise both naturally and from human sources during the burning of organic matter, are also leading causes of poor surface water quality. If these ubiquitous substances are omitted, only 3% of surface water bodies in Europe fail to achieve good chemical status.

Several other substances used in products enter surface water, mostly via urban waste water treatment plants. Examples are nonylphenols, used as surfactants, and the plasticiser DEHP.

Historically, pollution by metals was caused by industry and mining, but significant sources now include our homes, buildings and untreated storm water discharges. Agriculture is the major user of pesticides, though we have limited data to show that as a source, while municipal and domestic uses can be significant in urban waste water. The herbicides isoproturon, metolachlor, MCPA and terbuthylazine are discussed, as is the insecticide lindane, already heavily regulated but a very persistent and volatile substance. Some biocides, like tributyltin were used to protect vessels from "fouling" by mussels and other water organisms.

Chapter 4 considers some strategies and practical approaches as examples of the development of water and chemicals policies. The final chapter then draws some conclusions:

Most failures in chemical status of surface waters can be attributed to 3 groups of substances: mercury, PAHs and pBDEs. Specific actions targeting these priority substances are:

- Further effort to reduce emissions of mercury from urban waste water treatment plants, either upstream or before discharge, seems necessary.
- Improved understanding of pressures from emissions reporting needed to be able to implement effective measures to reduce pollution of water by PAHs.
- Improved understanding of the environmental pathways of pBDEs, to identify whether measures can be implemented which would limit further dispersal.

Emissions data on pollutants as reported in Europe (for WFD, E-PRTR or WISE-SoE) could give an important overview on emissions, impact of measures and trends. However, they are incomplete and inconsistent and too often exclude diffuse sources. Improvements to our understanding of emissions could be achieved by:

- Streamlining emissions reporting, so that robust data collected for one obligation would satisfy European emissions reporting requirements;
- Improvement in the monitoring and reporting of diffuse sources, to ensure that pressures are correctly understood and measures can be appropriately targeted.

For some priority substances, low numbers of water bodies failing to achieve good chemical status suggest that, assuming monitoring and reporting are accurate, measures have been effective in preventing the entry of these chemicals into surface waters. This is a success for European water and chemicals policies.

If these substances were no longer priority substances, resources spent on them could instead be used monitoring substances currently considered to present a risk.

The success of measures against gross chemical pollution means that we increasingly look to ensure the good ecological status of water bodies. Scientific advances have identified sub-lethal effects caused by chemicals which can harm the healthy functioning of an organism. Applying such techniques in the assessment of ecological status would be one way to improve protection from harmful chemicals under the WFD.

1.Introduction

1.1. Aim of this report

Like water, chemicals are an essential part of our daily lives. However, some present risks to plants and animals living in water, or the animals eating them. The risks presented by some chemicals have been recognised for decades, while those presented by others, alone or in combination, are continually being identified. Understanding which chemicals continue to pose significant risks in or via water, and why, can help to improve controls which minimise harm.

Techniques are now available which provide integrated measures of toxicity or harm, in contrast to established chemical methods which measure particular substances. The relationship between substance and source is fundamental to the system for chemicals regulation, yet that is under strain with the thousands of chemicals in daily use. Effect-based methods, which provide an integrated measure of the "chemical health" of the aquatic environment, could therefore offer a link between the ecological and chemical status of surface water bodies under the WFD. Describing some of these newer techniques and reviewing information about key pollutants under the WFD, this report gives both a grounding in what is known and a view of how surface waters might be better protected in future.

1.2. Structure of the report

Chapter 1 sets out the structure of this report and the legal background at European and international level. We now know much more about how chemicals can cause harm to organisms in water, and an overview of current knowledge is provided in chapter 2. In particular, sublethal effects (such as problems with reproduction) and mixtures of chemicals that in combination may act to harm sensitive species. Application of the precautionary principle would imply that this knowledge is used in risk assessment, to protect both the aquatic environment and human health. Chapter 3 goes on to consider what we actually know from data reported at European level, placed in the context of reporting under the Water Framework Directive. It reviews what we know about the pressures still causing surface water bodies to fail to achieve good chemical status, including information from European emissions reporting. Chapter 4 considers approaches to tackle with chemical pollution, looking at some EU and national strategies and plans. The final chapter then draws conclusions on what further needs to be done to protect surface waters from chemical pollution.

The scope of this report is hazardous substances, such as with toxic, persistent and bioaccumlative properties, not those that act as nutrients. The focus is on substances reported at European level, rather than emerging pollutants.

1.3. Context

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Action to address chemical pollution of water in Europe has been taken over several decades. The precautionary principle, enshrined in the Treaty of the Functioning of the European Union, underpins the approach to policy-making when an environmental or human health hazard is uncertain and the stakes are high (EPRS, 2015). Initial efforts to reduce gross industrial pollution of rivers and seas was followed by European legislation to limit sewage pollution. Scientific and public understanding of water pollution issues has increased and reports such as

EEA's "Late lessons from early warnings" served to highlight how information could be used to better protect human health and the environment (EEA 2001 and 2013).

The EU Water Framework Directive (WFD) aims to ensure good chemical status of both surface water and groundwater bodies across Europe. For surface waters, this goal is defined by limits on the concentration of certain pollutants relevant across the EU, known as priority substances. Good chemical status means that the concentrations of all priority substances do not exceed the environmental quality standards (EQS).

Comparison of the assessment on the status and pressures on Europe's waters under the WFD in the second cycle of River Basin Management Plan (RBMP) reporting (EEA, 2018a) with assessment results in the first cycle (EEA, 2012) shows marked improvements in the monitoring and classification of chemical status, with a clear reduction in water bodies in unknown chemical status. The percentage of surface water bodies in good chemical status within the EU is 38 %, while 46 % are not achieving good chemical status and 16 % of the water bodies have unknown chemical status.

In many Member States, relatively few substances are responsible for failure to achieve good chemical status. Mercury causes failure in a high number of water bodies. Omitting widespread pollution by ubiquitous priority substances including mercury, the proportion in good chemical status improves to 81 % of all water bodies, and 3 % do not achieve good chemical status and 16 % have unknown chemical status. The main pressures leading to failure of good chemical status are atmospheric deposition and discharges from urban wastewater treatment plants.

Since the first cycle of reporting of River Basin Management Plans (1st RBMPs) (EEA, 2012), Member States have made progress in tackling priority substances, significantly reducing the number of water bodies failing standards for substances such as several priority metals (cadmium, lead, and nickel) and pesticides.

The present report provides a more in-depth assessment on the key pollutants causing failure to achieve good chemical status of surface waters in the second cycle of RBMP reporting (2nd RBMPs), their sources and their ecological impacts in the aquatic environment. While surface waters in the WFD also covers transitional and coastal waters, we focus here on rivers and lakes.

In relation to hazardous substances, there has considerable activity in Europe, starting with the Programme of action of the European Communities on the environment in 1973 (EC, 1973). The 1976 Dangerous Substances Directive 76/464/EEC was implemented by Member States with action programmes on emissions and quality objectives as well as reporting activities. The Water Framework Directive (2000) provided an overarching approach to water management, including European and national prioritisation of pollutants, the Environmental Quality Standards Directive (EC, 2008a). EEA contributed with publications such as "Hazardous substances in Europe's fresh and marine waters" (EEA, 2011), European Waters 2012 (EEA, 2012) and ETC-ICM technical reports 3/2015 on hazardous substances and 3/2017 on emissions into Europe's Waters.

Box 1.1

Box 1.1: When pollution protection breaks down – cyanide

Cyanide is very toxic, inhibiting respiratory processes by irreversible binding to blood cells. It has been used in gold and silver mining, pigments (Prussian blue), biocides and in the production of textiles and pharmaceuticals. Natural processes create cyanides in fungi, plants and bacteria. Most cyanides in water originate from industry. Restrictions limit their use in the EU, owing to their high toxicity.

Serious pollution by cyanide occurred after an accident at a gold mine in Romania in 2000. Near Baia Mare a dam holding 300 000 m³ contaminated water with 100 t cyanide spilled into the Someş River, which flows into the Tisza (Ogul 2015). The spill contaminated the drinking water supplies of over 2.5 million Hungarians with catastrophic environmental consequences, killing over 1400 t fish.

Just as WFD provides a way to manage water across administrative boundaries, WFD chemicals bridges the legislation covering aquatic environment and chemicals source control. Considering the monitoring evidence collected under WFD can tell us about the effectiveness of source control legislation for the aquatic environment. This feedback for chemicals in water addresses a key information need, since most existing legislation for chemicals source control has no monitoring (e.g. REACH, biocides). It is also an opportunity to highlight the links along the Drivers-Pressures-State-Impacts-Responses (DPSIR) chain from the sources all the way into the aquatic environment, and possibly identify gaps in reporting obligations.

The report draws on additional data sources in particular from other reporting streams, e.g. for the European Pollutant Release and Transfer Register (E-PRTR) and the Urban Waste Water Treatment Directive. It also draws on the Water Information System for Europe State of Environment (WISE-SoE) reporting for emissions. Data for EEA member countries outside the EU have been incorporated where possible.

Monitoring requirements typically address well-known pollutants such as mercury, lead etc. This means that the availability of data for these substances should be relatively high, while information for most, more recently identified pollutants is much lower. Over recent years, scientific concern has risen in relation to the potential effects of mixtures of chemicals on aquatic life. There is particular concern in relation to substances designed to kill, such as pesticides, where combinations of substances at low concentration can be present in the same time and place. Advances in chemical analysis, using biological effects methods to take these combinations into account, can provide ways to identify risks to the environment.

Recent research linking chemical contamination with ecological effects in the aquatic environment is included in chapter 2, in particular from the European FP7 Research Project "Solutions for present and future emerging pollutants in land and water resources management"

(SOLUTIONS)¹. Some consideration of the research into new methods for chemical assessment, such as non-targeted screening and other integrative monitoring methods, is provided.

1.4. EU Policy context for chemicals in surface waters

Water Framework Directive:

The WFD entered into force on 22 December 2000, establishing a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater. Among the objectives of the WFD is the aim towards enhanced protection and improvement of the aquatic environment, through specific measures for priority substances. Priority substances are set out in the Environmental Quality Standards Directive (EC, 2008a), as substances presenting a significant risk to or via the aquatic environment.

The requirement to achieve good status in surface waters under the WFD means meeting certain standards for ecological and chemical status. "Good chemical status" means that concentrations of all priority substances in a water body are below the environmental quality standard (EQS) i.e. failure of one EQS means the water body does not achieve good status. These standards are set at European level. More local chemical standards, for substances discharged in significant quantities, can be set by Member States as "River Basin Specific Pollutants" (RBSPs) and contribute to the classification of ecological status.

Under the WFD, the Environmental Quality Standards Directive (EC, 2008a) concerns priority substances in surface waters. It defined environmental quality standards (EQS) which apply across the EU for the chemical status of surface waters, intended to limit the occurrence of certain chemical substances which pose a significant risk to the environment. Regular review of this directive includes review of the list of priority substances (Annex 10) to the WFD. This was firstly done in 2013 when 12 substances where added to the former 33 priority substances (and substance groups). Among the priority substances of the WFD some are defined as priority hazardous substances, which should be "phased out", i.e. all discharges, emissions and losses must be ceased².

Art. 7 of the WFD is targeted at protecting human health. If the drinking water standard is exceeded at the tap and water was taken from surface waters, specific measures need to be taken for the affected water bodies to guarantee compliance with the drinking water standard. This approach updated the drinking water standard for pesticides and biocides, set in 1980.

¹ http://www.solutions-project.eu/project/

² While introducing this comprehensive concept, the WFD repealed the former Dangerous Substances Directive (EC, 2006a).

Other EU legislation on water protection concerning chemicals:

- The Urban Waste Water Treatment Directive (EEC, 1991a) obliged Member States to collect and treat wastewater from households and small businesses, and aimed to reduce organic pollution as well as nitrate and phosphorus discharges from these sources. It ended the dumping of sewage sludge to surface waters in 1998, reducing a significant source of hazardous substances in water.
- The Nitrates Directive (EEC, 1991b) regulated fertilizers and served to reduce nutrient inputs from agriculture, especially from intensive livestock forming. (Nitrate is not a pollutant covered in this report.)
- The Drinking Water Directive (EEC, 1998) set special quality requirements for water for human consumption. It set concentration limits for a range of hazardous substances, including total "pesticides", benzo(a)pyrene, cadmium, lead, mercury, nickel and PAHs, in drinking water. Some of these limits were based on analytical detection limits at the time.
- The Marine Strategy Framework Directive (MSFD) (EC, 2008b) defined the target of achieving or maintaining a good environmental status of the EU's marine waters by 2020. For pollution, it sets two qualitative descriptions of the marine environment when good environmental status has been achieved. Descriptor 8 sets out that concentrations of contaminants give no effects and Descriptor 9 that contaminants in seafood are below safe levels.

In addition to the water protection directives described above, there are various other polices and regulations that are not specifically aimed at protecting the environmental medium "water", but are significant concerning chemicals in water:

- The Industrial Emissions Directive (EC, 2010) sets out rules on integrated prevention and control of pollution arising from selected industrial activities.
- The PRTR Regulation (EC, 2006b) regulated the reporting requirements and supply of data to the EU for a European Pollutant Register, providing access to information on pollution. Operators must report emissions of pollutants if those exceed specified thresholds.
- The Plants Protection Products Regulation (EC, 2009a) set out rules for the authorisation of plant protection products and their marketing, use and control.
- The Directive on the sustainable use of pesticides (EC, 2009b) aims at reducing the risks and impacts of pesticide use on human health and the environment, and promoting the use of integrated pest management and alternatives such as non-chemical approaches.
- The Biocide Regulation on the marketing and use of biocide products (EU, 2012).
- The Sewage Sludge Directive (EEC, 1986) regulated the use of sewage sludge in agriculture to prevent harmful effects.
- The 7th Environment Action Plan (EU, 2013a) set the objective that by 2020, use of plant protection products should not have any harmful effects on human health or unacceptable influence on the environment, and such products should be used sustainably.
- The Medicinal Products Regulation (EC, 2004) laid down Community procedures for the authorisation, supervision and pharmacovigilance of medicinal products for human and veterinary use.
- REACH (EC, 2007) addressed production and use of chemical substances and regulates the assessment of their impacts on human health and the environment.

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- The Classification, Labelling and Packaging Regulation (CLP) for chemicals substances and mixtures complemented REACH (EC, 2008c).
- The Strategic Environmental Assessment Directive (EC, 2001) defined, that for large programmes, environmental impact assessment needs to be applied at an early stage of planning with a view to promoting sustainable development.
- The basis for environmental impact assessment (EIA) under European Community law provided the EIA Directive (EU, 2011). It prescribed the individual process stages of EIA and the project types for which an EIA must be carried out.
- Regarding facilities that handle substances dangerous to water, an important part is also played by the EU Directive on the control of major-accident hazards involving dangerous substances (EEC, 1982), the Construction Products Directive (EC, 1989) and the standardisation procedure under CEN (Comité Européen de Normalisation).

EEA member countries which are not members of the EU with environment and water law comparable to those with the EU include Iceland, Liechtenstein, Norway and Switzerland.

In addition, international agreements exist to limit the harm caused by particular chemicals:

- The Stockholm POPs Convention³, effective from May 2004, aims to eliminate or restrict the production and use of persistent organic pollutants (POPs), such as several polybrominated diphenylethers and several hexachlorocyclohexane isomers (including lindane), which are addressed later in this report.
- The Minamata Convention⁴ on mercury came into force in 2017, and is designed to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds.
- The International Commission for the Protection of the Danube River⁵ is a collaboration of 14 countries. It aims to promote and coordinate sustainable and equitable water management, including conservation, improvement and rational use of waters for the benefit of the Danube River Basin countries and their people.
- The Convention on the Protection of the Rhine⁶ is a cooperation between the 5 countries bordering the Rhine river, aiming at the preservation, improvement and sustainable development of the ecosystem.
- The International Commission for the Protection of the Elbe River⁷ aims to promote the use of water, achieve the most natural ecosystem possible and decrease the burden on the North Sea.

This long list demonstrates the critical role that water plays in the environment and human health.

Chemicals in Europe's surface waters

³ http://www.pops.int/ (31/03/2018)

http://www.mercuryconvention.org/ (31/03/2018)

⁵ https://www.icpdr.org/main/ (28/082018)

⁶ https://www.iksr.org/en/international-cooperation/legal-basis/convention/ (28/082018)

⁷ https://www.ikse-mkol.org/en/ikse/fokus-2015/ (28/082018)

2. "Known unknowns" – unregulated micropollutants and chemical mixtures

2.1. Introduction

Under the WFD, surface water assessment is separated into chemical and ecological status. Such separation may reflect a practical solution for water regulation but it is artificial for the environment. This chapter considers ways to gain evidence for better linking chemical and ecological status of surface waters in future.

Following the reduction of gross pollution, considerable effort in recent years has been put into developing ways to assess the impact of chemicals from an organism's perspective i.e. "what concentrations of which substances affect the healthy functioning of an ecosystem?" A better understanding could allow improved targeting of measures to reduce harmful concentrations of pollutants. Alongside this, concerns have grown about the "cocktail effect" – mixtures of low concentration chemicals which in combination may cause harm. Some of the challenges and proposed solutions towards improving assessment of chemical risks in water are considered below.

2.2. Chemical and ecological status

The Water Framework Directive (WFD) assesses chemical and ecological status of surface water bodies separately. However, organisms living in the water experience an integration of all the influences present. The different statuses can lead to the criticism that the reported "chemical status" may be remote from what is actually occurring in the water ecosystem.

The chemical status of surface waters under the WFD is based on a comparison of measured concentrations of EU-wide consented priority substances with target levels established under the Environmental Quality Standards Directive (EC, 2008a). Ecological status is assessed from monitoring data on biological quality elements (BQE) such as benthic invertebrate fauna, phytoplankton, macrophytes, and fish. Additionally, data on hydromorphology (physical characteristics), physico-chemical water parameters and RBSPs can be used (figure 4.1). Owing to the particular geographic circumstances of any particular water body, assessment of ecological status is made with reference to specific local factors.

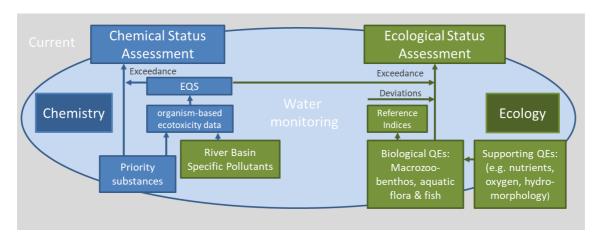


Figure 2.1: Overview on the current status assessment approach under the WFD

The value of chemical measurements in rivers and lakes is that they allow direct comparison of concentrations between sites. Furthermore, they can be related to emission loads and, therefore, controls can be directed towards specific sources of chemical pollution. However, among the criticisms of this approach are that ecological structures and functions, key targets of chemical pollution, can be poorly related to specific chemical measurements. In particular, pollution by emerging compounds may be overlooked.

Efforts to link chemical occurrence and ecological effects are not required under the WFD and failures to achieve good ecological status, solely driven by chemical pollution (e.g. RBSPs), are rarely observed.

Fig 2.2a-d shows chemical status with and without uPBTs, as well as the ecological status, by country.

Figure 2.2a shows chemical status by country (EEA, 2018a). A number of countries have reported 100% failure of chemical status owing mainly to pollution by mercury. The 2013 Priority Substances Directive (EU, 2013b) identified 4 groups of substances as "ubiquitous, persistent, bioaccumulative and toxic" (uPBT) (section 1.2). Omitting these from the calculation of chemical status increased overall good chemical status to 81% ((graph C). Meanwhile, ecological status is shown in graph B.

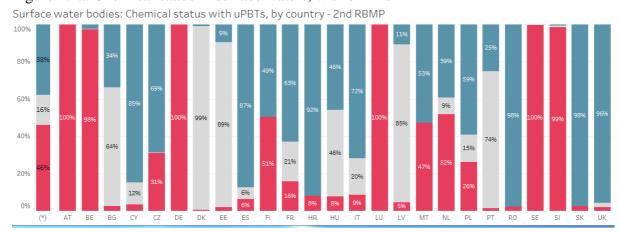


Figure 2.2a: Chemical status in surface waters, with uPBTs

Figure 2.2b: Chemical status in surface waters, without uPBTs

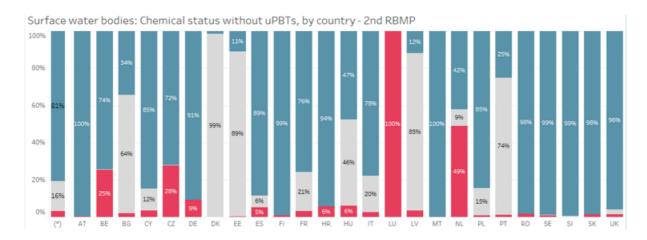


Figure 2.2c: Ecological status in surface waters

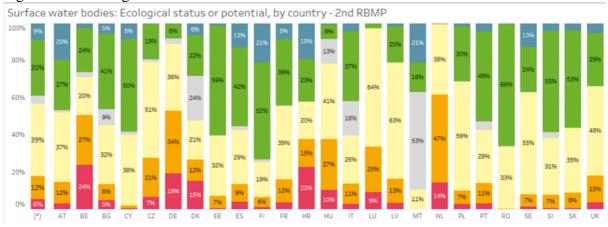
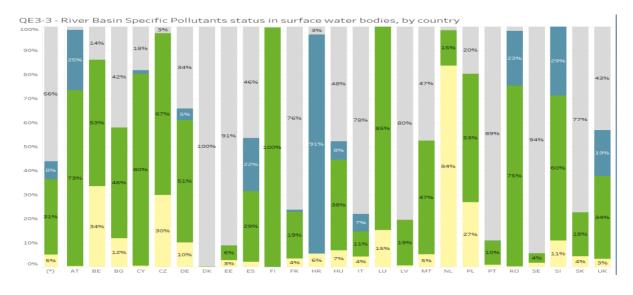


Figure 2.2d: Status of RBSPs,





It is difficult to see what relationship, if any, exists between figures 2.1A-C. It can also be seen that in many water bodies, the RBSPs have not been reported in the assessment of ecological status (Fig 2.1D).

Information on whether and to what extent chemical and ecological status indicators are correlated has the potential to be used to indicate the effects of pressures and, potentially, explain causes of observed ecological effects, providing evidence for decision-makers. The scientific community has proposed diagnostic approaches to unravel links between ecological effects and chemical contamination, and strong interest in this research has been indicated by stakeholders of water management (Brack *et al.* 2015) (Box 2.1).

Box 2.1

SOLUTIONS – pollutants in land and water management

This EU FP 7 project assessed how existing WFD practice could be brought more upto date with currently available scientific knowledge (Brack et al. 2017). Recommendations included:

- use of effect-based methods for pollution investigation and assessment
- use of passive sampling for bioaccumulative pollutants
- integrated strategy for prioritisation of contaminants in monitoring
- consideration of priority mixtures of chemicals
- historical burdens accumulated in sediments
- models to fill data gaps
- tiered approach in investigative monitoring to identify key toxicants

https://www.solutions-project.eu/project/

2.3. Evidence for chemical pollution causing ecological effects

The established way of identifying clear links between a chemical and its effect on organisms is through concentration-response relationships, for example by comparing an organism's health response with increasing concentrations of a chemical. As it is impossible to assess the sensitivity of all organisms to all pollutants, assessment factors are applied to accommodate for uncertainties and data gaps, including chronic effects. Where an EQS has not been

established for a substance, experimentally-derived effect concentrations may be compared with estimated or measured environmental concentrations (figure 2.2).

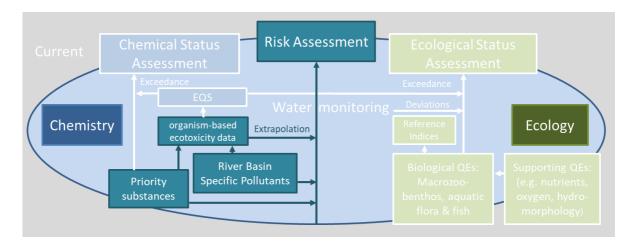


Figure 2.2: Individual chemical risk assessment is based on comparison of single chemicals concentrations in the environment with standards, which are derived from measured effect concentrations by using extrapolation factors to account for uncertainties and data gaps.

Box 2.2 Definitions

Acute toxicity – adverse effect on an organism after short-term exposure.

Chronic toxicity – adverse long-term effect after long-term exposure (typically at lower concentrations than those causing acute toxicity).

Mixture toxicity – adverse combined effect after exposure to multiple pollutants

Mode of action – understanding of how a chemical acts in an organism or ecosystem

Bioassay – biological test system (organism or cells)

Effect based method (EBM) – bioassay suitable for environmental monitoring

Molecular target - biomolecule (e.g. protein) that directly interacts / binds with a chemical

A pioneering study by Malaj *et al.* (2014) used monitoring data on chemical concentrations, based on data reported in WISE–SoE. The authors considered more than 200 substances monitored in European freshwater systems. They reported an acute risk at 14% and a chronic risk at 42% of the sites investigated (figure 2.3 A). One issue identified using this approach, however, is that the expected risk increases with the availability of chemical monitoring data. Where concentrations are unknown, they cannot be used in the assessment and so this may

result in a skewed result, with sites for which information is available appearing worse than those for which this information is not provided (figure 2.3 B). A further issue is that the availability of data for acute toxicity is much greater than that for chronic toxicity, meaning that the chronic risk assessment is more dependent on assessment factors and thus prone to larger errors.

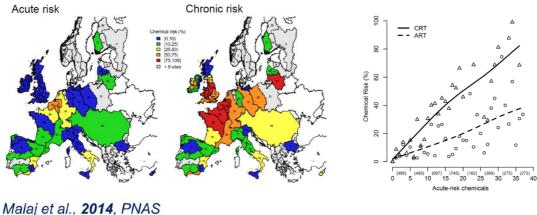


Figure 2.3: A) Acute and chronic risk estimates for European water bodies based on reported chemical monitoring data and calculated using risk estimates for individual compounds; B) Correlation between chemical risk and number of chemicals analysed for acute risk (ART = acute risk threshold, CRT = chronic risk threshold); figures from Malaj et al. 2014)

Recent research indicates that chemicals contribute to a significant but varying extent to the total effective stress in river ecosystems (Schäfer et al. 2016, Rico et al. 2017). Rico and colleagues (2016) showed that variation in invertebrate communities could be mainly explained by habitat and water quality, with physico-chemical parameters (e.g. dissolved oxygen) explained more of the variation than metals or organic contaminants. The authors reported that it was difficult to find direct links between individual contaminants and ecological effects.

In the EEA's RBMP Assessment (EEA, 2018a), it is highlighted that countries with good ecological status for benthic invertebrates also have lower levels of pressures. This seems true especially for diffuse pollution and hydromorphological pressures. To identify e.g. pressurerelated failures of good ecological and chemical status might require a second line of assessment, beyond the prevailing basic one-out all-out principle. Such studies could be successful with pollutant concentrations instead of EQS exceedances and organism compositions instead of biological quality element classes.

In conclusion, it is rarely possible to explain observed effects in ecosystems based on knowledge about the presence of individual chemicals, while ecological impact information alone is similarly not sufficient to identify the chemicals causing that impact. Instead multiple lines of evidence are needed.

Dealing with mixtures of chemicals

For establishing causal relationships between chemical pollution and ecological effects, it has to be appreciated that in the real world there are no cases where only a single substance occurs in the environment. Emissions data and research show that the aquatic environment has to deal with mixtures of chemicals, which contain many more substances than just the priority substances. Nutrients from urban point sources, agricultural diffuse pollution, metals from stormwaters from cities and atmospheric deposition, as well as many potentially harmful organic chemicals from urban waste water and agriculture, have been shown to be present in freshwater systems simultaneously. Indeed, scientific monitoring approaches highlighted the co-occurrence of hundreds of chemicals in different freshwater bodies (e.g. Loos *et al.* 2009 & 2013, Moschet *et al.* 2014). This complexity mismatches with the single substance approach of current chemicals assessment under the WFD.

The occurrence of chemical mixtures in freshwater systems is the result of different sources and different patterns in time, space and concentration (e.g. Baker & Kasprzyk-Hordern 2013, Beckers *et al.* 2018) and so does the respective risk for the ecosystems. The challenge is to figure out which of the many substances present are most important for the toxicity of a mixture.

Efforts exist to simplify this complicated picture. In essence, these aim to separate and categorize the issues of pollution, impact and identification of key chemicals to achieve a problem-targeted assessment (figure 2.4). Statistical methods are used to characterise complex pollution situations and relate these to sources (Posthuma *et al.* 2017). This approach offers the potential for identifying categories of mixture: "typical" i.e commonly-occurring, or "priority" i.e. containing substances which are of particular concern in a mixture, for instance because they promote toxicity. This is particularly relevant for the diverse and numerous organic micropollutants for which single representative candidates on lists of regulated substances are often outdated or may be substituted by substances with potentially similar toxicity when regulation comes into play. The combined action of similar compounds occurring together is not captured at all (Altenburger *et al.* 2015).

Examples for co-occurrence of similar compounds comprise the neonicotinoid insecticides imidacloprid, thiacloprid, acetamiprid which have been shown to occur simultaneously in water bodies but also antibiotic drugs such as azithromycin, erythromycin, and clarithromycin or the herbicides (e.g. diuron and isoproturon).

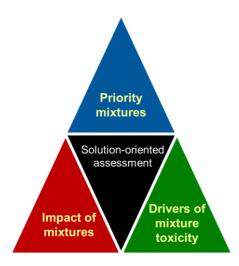


Figure 2.4: Dealing with mixtures in water management through differentiation into pollution (priority mixtures), effect (impact of mixtures) and risk (drivers of mixture toxicity) issues (modified from Altenburger *et al.* 2015)

A study by Busch et al. (2016) described the diversity of potential molecular targets for contaminant-biosystem interactions. In this study 426 organic chemicals were summarized to be detected in European freshwaters,

containing 173 pesticides, 128 pharmaceuticals, 69 industrial chemicals and 56 other compounds. These targeted more than 100 different biological molecules known to exist in aquatic organisms. This complicated picture was simplified by considering the ways in which

the chemicals acted upon organisms – "modes-of-action". 30 mode-of-action categories were identified for freshwater contaminants (figure 2.5), so that even with a potentially unlimited number of chemicals, there is a limited range of adverse biological effects. This approach could be used to simplify toxicity assessment.

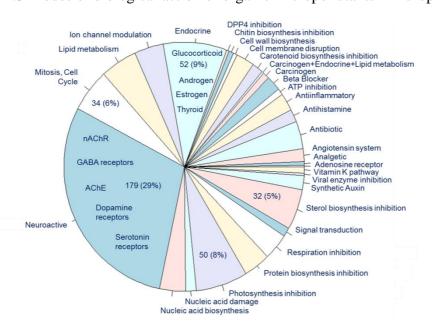


Figure 2.5 Modes of biological action of organic micropollutants in European freshwaters

Source: Busch et al. 2016)

Notes: Abbreviations: GABA – gamma-Aminobutyric acid (chief inhibitory neurotransmitter in the mammalian central nervous system); nAChR - nicotinic acetylcholine receptor (see table 3.1); ATP – adenosine triphosphate (energy carrier in the cells of all known organisms), DPP4 - Dipeptidyl peptidase-4 (an enzyme)

The largest group of organic micropollutants with a known mode of action identified in this study were neuroactive compounds, which affect or interact directly with the nervous system. Chemicals that affect the nervous system interact with different molecular targets, e.g. different insecticides binding either to the nicotinic acetylcholine receptor or inhibiting the enzyme named acetylcholine esterase (table 2.1). Both affect the signalling in the nervous system and mixtures of such chemicals will enhance the effects. Aquatic invertebrates might be particularly at risk owing to exposure to mixtures of different kinds of insecticides, while other species, such as fish, might be affected by the presence of antidepressant or antiepileptic pharmaceuticals that affect the nervous system of fish, possibly in combination with effects caused by insecticides. This means that chemicals, such as pesticides and pharmaceuticals, which are intended to act via certain modes of action in a certain species, can affect other species as well. For industrial chemicals, such as bisphenol A, PAHs and pBDEs, it is rather difficult to define a specific mode of toxicological action as those can show complex and multiple modes of action. They have been found to cause different chronically relevant responses, indicating long term toxicity such as endocrine disruption and mutagenicity, across various organisms including humans.

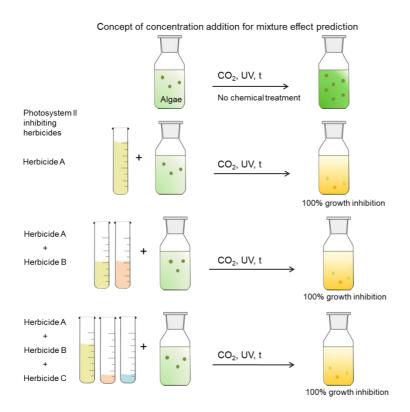
Table 2.1: Examples for mode-of-action categories and related mechanisms of chemical action (*For further details see Busch et al. 2016*)

Mode of action category	Mechanism	Chemicals known to act on/through this pathway		
Neuroactive perturbation: Chemicals interacting with the nervous system	Acetylcholine esterase (AChE) inhibition: AChE is an enzyme responsible for the depletion of the neurotransmitter acetylcholine; inhibition of AChE leads to increasing levels of this neurotransmitter and finally to an disruption of the nervous system signalling	Organophosphate insecticides, e.g. chlorpyrifos, diazinon		
	Interaction with nicotinic acetylcholine receptor (nAChR): nAChR proteins respond to the neurotransmitter acetylcholine, chemicals, that bind to nAChRs, disrupting neurotransmission	Neonicotinoid insecticides, e.g. imidacloprid, thiamethoxam		
Photosynthesis or plant growth inhibition: Chemicals disrupting	Photosystem II (PSII) inhibition: inhibition of PSII proteins leads to energy breakdown and cell death	Specific herbicides, e.g. diuron, isoproturon, atrazine		
processes in plants relevant for energy self-regulation, growth, and development	Gibberellin pathway disruption: Gibberellins are plant hormones that regulate growth and are involved in processes related to development and reproduction	Specific herbicides, e.g. alachlor, metolachlor		
Endocrine disruption: Chemicals interacting with the hormone system of animals and humans	Estrogenic disruption: Chemicals activating or inhibiting proteins of the estrogen pathway, such as the estrogen receptor, can cause chronic effects in organisms and populations leading to problems in reproduction.	Specific pharmaceuticals, e.g. 17β-estradiol, several industrial chemicals, e.g. bisphenol A, 4-nonylphenol		
	Thyroid disruption: Chemicals activating or inhibiting proteins for production, transportation, and metabolism of thyroid hormones can cause chronic effects on reproduction, development and metabolism in organisms and populations.	Specific pharmaceuticals, e.g. carbimazole, several industrial chemicals, e.g. DDT, bisphenol A, PCBs, PBDEs		

It can be difficult to predict the outcome of chemical mixtures on biological effects. In broad terms, the chemicals might a) act independently of each other, exhibiting individual toxicity; b) in combination, be more toxic, as a summed total of the individual chemicals or more toxic than that; c) be less toxic as the chemicals interfere with each other in toxicity mechanisms. For chemicals in a mixture that have the same mode of action, an additive combination effect

may be expected (Altenburger *et al.* 2015, Figure 2.6). Developing knowledge in this way, considering effect contributions from all compounds detected, would be expected to provide stronger association between chemical and ecological assessments.

Figure 2.6 Predicting the outcomes of mixtures - concentration addition for compounds with the same mode of action.



2.5. Examples combining chemical and biological monitoring

While modern effect-based methods have been proposed for mixture assessment, as a complement to chemical and ecological monitoring, precedent already exists in this respect. Such methods offer something similar to the "biological oxygen demand" (BOD) which measures an overall condition in the water while not specifying the cause. Despite this lack of specificity, BOD is widely used in water management to protect surface waters (EEC, 1991; EC, 2000).

Currently, there are few requirements to use effect-based information in regulatory assessment. An example where effect-based monitoring is used for assessment is the Marine Strategy Framework Directive (EC, 2008b). Different descriptors of good environmental status, such as "concentrations of contaminants at levels not giving rise to pollution effects", are defined and the assessment allows the integration of data on biological effects (Lyons *et al.* 2017). The application of bioassays for measuring the occurrence of dioxins and PCBs in foodstuffs (EU 2012) demonstrates how effect-based assessment might operate in a regulatory framework. The value of such information is that it integrates the effect of mixtures of chemicals irrespective of whether the combined effects are additive or different from an expectation.

For example, the total potency of compounds with estrogenic activity in a water sample can be determined by measuring the activity of the estrogen receptor in laboratory *in vitro* assays. Ideally, the bioassay captures the total effect of all chemicals with estrogenic effect in a sample. Practically, difficulties exist, though the robustness of techniques has improved for some modes of action in recent years (e.g. Altenburger *et al.* 2018, Leusch *et al.* 2018, Kunz *et al.* 2017).

For regulatory monitoring, techniques need to be robust and reliable, to meet legal challenge and ensure that investments are based on sound evidence. A series of International Standards Organisation (ISO) standardized methods is available for the use of biological methods for the assessment of effluents on water quality⁸. The EU water directives transposed into national regulation allow Member States to set requirements appropriate for the country level e.g. the German "Abwasserverordnung" (AbwV, 1997) specifies standard methods for specified types of waste waters.

To demonstrate the application of biological effect tools in monitoring, case studies have been undertaken. In a pilot study by Escher *et al.* (2014) the efficacy of different waste water treatments was determined using the observable effects of enriched water samples in about 100 different miniaturized and mainly cell-based bioassays (figure 2.6). Results showed the presence of different chemicals at different levels of pollution with diverse modes of action.

Figure 2.6: Examples of organism and cell-based bioassays for water monitoring; scientists handling samples in front of an automated sampling device



In a case study performed within the European FP7 project SOLUTIONS, Neale and colleagues (2017) investigated the WWTP effluent, upstream, and downstream river water samples in Switzerland. They compared bioanalytical results from 13 bioassays with results from chemical analysis of 405 compounds (see figure 2.7 A). They found that of the 10 detected herbicides known to inhibit the photosystem II (PSII), terbuthylazine and diuron could explain the majority of biological effects (figure 2.7 B). The authors also showed that the detected chemicals could explain between 45 and 108 % of the observed biological effects. In samples collected upstream of the WWTP, only a fraction of the total measured effect could be explained by the detected chemicals.

⁸ https://www.iso.org/committee/52972/x/catalogue/

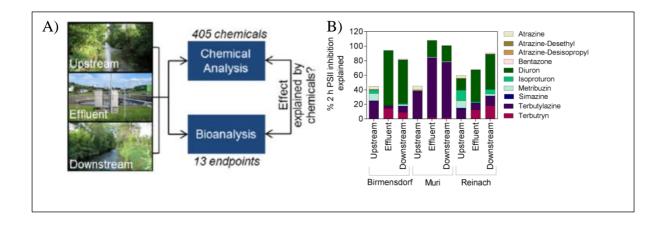


Figure 2.7: Example of a comparative analysis of chemicals and combined effects using component-based mixture predictions (taken from Neale *et al.* 2017)

2.6. Towards effect-based methods in monitoring and assessment

Assessment under the WFD currently does not consider mixture effects. It is, therefore, possible that concentrations of priority substances could be slightly below their respective EQS, meeting good chemical status, while the actual combination of substances present could be harmful. For example, if all five PSII inhibitors from the priority substances list were detected, individual concentrations might be at good chemical status but the mixture could nevertheless cause adverse effects (Figure 2.6). Additionally, while the list of priority substances represents certain hazardous chemicals, there are other substances present in surface waters which could contribute to mixture effects.

Mixture effect considerations could thus be integrated into the existing assessment schemes following two approaches that could be anticipated:

Compound-based mixture prediction: EQS for mixtures of similar acting compounds could be established and potentially considered in chemical status assessment.

For example, an EQS for the sum of all six PSII-inhibitors could be defined as the sum of the single substance concentrations divided by the single substance EQS. If this sum exceeds "one", than the EQS of priority PSII-inhibitors is exceeded.

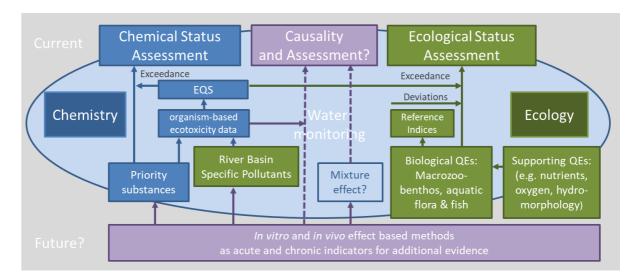
Mixture effect detection using effect-based methods: Joint effects measured with a bioassay instead or in addition to single chemical compound concentrations might be considered as indicators for the ecological status assessment.

For example, instead of determining the concentrations of each PSII inhibitor in a water sample, the sample would be concentrated and tested in a dilution series using a bioassay (e.g. algae growth inhibition test). At the point where the toxicity ceases, the dilution factor would be compared with the test result of a defined reference compound (e.g. diuron).

Currently, several whole organism-based assays and some cell-based assays are ready for routine use in an effect-based monitoring. Readiness for use implies fulfilling requirements regarding standardization, robustness, reproducibility - for several modes of action, we lack specific bioassays, even though there are many techniques available to researchers. Within the WFD water quality assessment, selection of the relevant bioassay could be derived from the

biological quality elements assessed in the water body. Organism-based bioassays therefore could support the link between chemical and ecological monitoring and assessment (figure 2.8).

Figure 2.8: Biological effect assessment could serve to close the gap between ecological and chemical assessments and gain causal relationships



The European Commission (Wernersson et al. 2015) gives a summary of available bioanalytical tools in the technical report on aquatic effect-based monitoring tools under the WFD. Their readiness for monitoring applications has been evaluated in several projects (e.g. Kienle et al. 2015). These tools can be applied and used in a modular manner depending and targeted on the desired level of evidence (figure 2.9).

Two applications of effect-based methods can be foreseen:

- The monitoring of chemical impact on biological quality elements (BOEs). For effect monitoring, a module comprising different organism-based bioassays representing the different BQEs would provide evidence for total chemical impact. It would also enable direct linkage of effect observations with ecological monitoring data (figure 2.9 A, figure 2.8). However, to detect chemicals with an impact that emerge over a longer time scale, such as endocrine disruptors or mutagenic and genotoxic compounds, additional bioassays, such as cell-based mutagenicity assays and estrogen receptor activation assays should also be implemented (figure 2.9 B).
- Investigations of pollutants which cause effects. When investigating chemicals which could be causing effects through specific modes of action (table 2.1) or on specific, stress-related endpoints, additional bioassays are available (figure 2.9 C&D). The application of such in vitro detectors may also be used to protect specific uses of a water body, e.g. drinking water abstraction.

Figure 2.9: Modular approach for application of bioassays in monitoring

	Module based Bioassay Battery for Monitoring	
Monitoring	 Algae growth inhibition test A) Integrated effects bioassays (related to WFD BQE) Water flea immobilization test Fish embryo toxicity test)
	 Cell based assays detecting mutagenicity and/or genotoxicity indicative for chronic effects Receptor based assays detecting endocrine activity (e.g. ER, AR, TR))
	C) Bioassays Indicative for specific groups of compounds (via known MoA) Photosynthesis inhibition test AChE inhibition test EROD assay	Diagnosis
	D) Additional bioassays indicative for specific molecular responses Additional receptor based assays (AhR, GR, PPARγ, PXR, etc.) Additional bioassays indicative for inflammation, oxidative stress, etc.	Diag

2.7. Challenges

The implementation of effect-based methods into monitoring routines or diagnostic screening approaches would require agreement on the bioassays to be used. Robust bioassays have been developed for some organisms (such as invertebrates like *Daphnia*) and assays for the detection of estrogenic compounds, with detailed recommendations for application in monitoring (e.g. Kunz *et al.* 2017).

Broadening the use of analytical techniques to better link chemical and ecological status assessment under the WFD is summarized in figure 2.10.

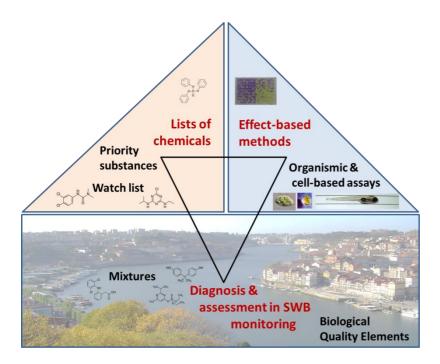


Figure 2.10: Smart combination of existing approaches for characterizing a water body can support the understanding of connections between chemical contamination and ecological status

Clearly, there are limitations as to what can be reasonably expected from such efforts, with both scientific and practical considerations, such as:

- i) Chemical analysis of freshwaters is limited to what has been looked for, be that through targeted, screening or untargeted analytical strategies. The limitations are specific for each approach;
- ii) Complementary use of effect-based methods needs to consider which tests should be used:
- iii) Effect based Methods rely on concentrating the dissolved substances in a water sample through solid phase extraction methods. Such methods work well for some organic compounds (non-polar) but not for others (e.g. polar compounds including glyphosate and AMPA) (Reemtsma *et al.* 2016). Neither metals nor contaminants bound to particles will be detected by the effect-based methods discussed and would thus need separate analysis. This is a significant omission given the relatively widespread failure of metal EQSs (EEA, 2018a; Johnson *et al.* 2017).

2.8. Summary

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The major advantage of incorporating mixture assessment and biological effect detection is that the effects of chemical pollution can be identified more comprehensively, allowing further bridging between chemical and ecological status.

Most effects-based methods do not provide conclusive evidence of the chemical(s) responsible. That requires further, site-specific effort, which is where scientific technique bumps into a regulatory approach based on individual substances. Water managers need to, firstly, identify which components of the mixture are the main contributors to the harmful effects, and

secondly, to reduce those inputs. However, this approach is not entirely new – "biological oxygen demand" (BOD) has been used many years as an integrated measure of water pollution.

In relation to chemical status assessment under WFD, the inclusion of techniques more sensitive to chemical pollution is likely to make it more difficult to achieve good chemical status. While this situation may reflect expert opinion based on current scientific knowledge as to "real chemical status" it would represent further difficulties in communicating progress under the WFD. One option could be for effects-based methods to be used as part of ecological status assessment.

3. Known risks: Key pollutants and their sources

3.1. Introduction

At European level, our knowledge of the chemical status of water is largely based on regulatory requirements, which demand information on well-established, key pollutants. In the WFD, most priority substances are already subject to use restrictions under REACH or pesticides legislation, while river basin specific pollutants (RBSPs) are usually subject to national legislation. So why do we still see failures to achieve good status for these substances? This chapter considers key chemical pollutants and why these continue to pose challenges to good water quality in Europe.

When the assessment of status under the WFD finds a failure, the reasons for that – the "pressures" need to be investigated, as a step towards identifying measures that might be taken to bring the water body to good status. Therefore, here we consider the priority substances most frequently causing failure to achieve good chemical status, and RBSPs most frequently causing failure to achieve good ecological status. For example, improved waste water treatment or altering farming practice can help to reduce harmful chemicals reaching the aquatic environment.

It is important to appreciate that this is where WFD meets chemical source control legislation. Environmental monitoring undertaken for WFD feeds back information to legislation such as REACH, on the effectiveness of the source control. However, because some chemicals are persistent and can remain in the environment for a long time, we also need information on the trend, to assess whether and how concentrations are changing. At a European level, there is limited comparable information about concentrations of hazardous substances over time. To get around that issue, reporting on the trends in chemical emissions can provide complementary information on the status of chemicals in the environment. For the key priority substances, emission data reported under the E-PRTR, WFD and WISE State of Environment reporting are presented. Conclusions about our level of understanding and areas where actions need to be taken, are provided.

3.2. Chemical Status, River Basin Specific Pollutants and Pollutants most frequently exceeding standards in Europe

Under the Water Framework Directive, the chemical status of surface waters is assessed against environmental quality standards (EQSs) for a list of priority substances. EQSs are set to protect the most sensitive species – this could be e.g. algae or invertebrates but also top predators like fish or humans, which may eat many smaller organisms and cause the pollutant to "bioaccumulate". The first list of priority substances included 33 substances and groups in the

Environmental Quality Standards Directive (2008/105/EC). The list of priority substances was updated with the Priority Substances Directive (2013/39/EC)⁹.

A summary of findings for chemical status of surface waters from the recent RBMP assessment is provided in Box 3.1 (EEA, 2018a).

Box 3.1¹: Key messages on chemical pollutants from EEA'S RBMP Assessment, 2018

- The WFD data reported by Member States showed that 38% of the surface water bodies within the EU were in good chemical status, while 46% were not in good status and for 16%, the status was reported as 'unknown'. Compared to the previous assessment results in 2010, the number of water bodies with unknown status had decreased significantly (minus 25%), yet the improvements in chemical status were limited.
- In particular, mercury and polybrominated diphenylethers (used as flame-retardants) caused significant failure to achieve good chemical status in surface waters. Mercury and PAHs now mainly reach the aquatic environment following atmospheric deposition, whereas contamination with cadmium, lead and nickel is caused by discharges from waste water treatment plants or from historic mining areas. As well as the use, the pathway taken by the substance to reach the water body influences the relative difficulty of preventing pollution.
- It seems that for substances such as metals (cadmium, lead, and nickel) and several pesticides, some effective measures have been implemented, with Member States reporting improved status for these substances in some water bodies.
- RBSPs also show chemical contamination, but are regulated under ecological status with regional or national EQS. 5 % of surface water bodies did not achieve good ecological status owing to RBSPs, with 40 % reported as being in good or high ecological status, although 55%, the status of RBSPs was unknown.
- About 165¹ RBSPs were reported as causing failure to achieve good ecological status in at least one water body. Those most frequently reported as causing failure were the metals zinc, with 1503 waterbodies failing to achieve good ecological status, and copper (845). Other types of substances causing most failures were ammonium and elements such as arsenic and selenium. As individual substances, most RBSPs caused fewer than 100 waterbodies to fail good ecological status.
- There are differences in the numbers of substances defined by countries as RBSPs (between 5 and over 300) and differences in environmental quality standards applied. This means comparison between countries should be undertaken with care.
- Of the thousands of chemicals in use and potentially present in surface waters, relatively few have been identified as causing failure. From the information reported, it is not known how many other chemical pollutants are present in surface waters, and whether their concentrations should be of concern.

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^{1 -} Numbers updated as at 30/0/2018

⁹ The 2013 Priority Substances Directive contains a revised list of 45 priority substances and groups of substances. In the EEA status and pressures assessment (EEA, 2018a), Member States were required to use report using the 2008 EQSs, though some applied a more stringent approach, using the 2013 EQSs.

Examining these findings further, the priority substances and RBSPs most often exceeding environmental standards under the recent WFD reporting are shown in Table 3.1. This table shows the priority substances and most of the RBSPs which caused failure in at least 4 Member States¹⁰. To better understand the pressures causing particular chemicals to cause failure of good status, they are grouped according to the main pressure or pathway generally understood for that substance to reach the aquatic environment. Substances have been included, when exceedances were reported from at least four Member States.

¹⁰ A further six natural chemical elements exceeded standards for RBSP in at least four Member States (Barium, Selenium, Boron, Cobalt, Uranium, Thallium)

Table 3.1: List of pollutants most frequently exceeding EQS in surface water bodies in EU25 (out of 111 105 water bodies)

Pollutant	Type / Use of chemical	No. of Member States with EQS exceedance	No. of water bodies with EQS exceedance(a)	Priority substance (PS) / RBSP (a)			
Contamination mainly through atmospheric deposition (section 3.4)							
Mercury	Metal	22	45 739	PS(b,c)			
Benzo(g,h,i)perylene + Indeno(1,2,3-cd)-pyrene	PAH	13	3 080	PS(b,c)			
Fluoranthene	PAH	13	1 324	PS			
Benzo(a)pyrene	PAH	11	1 627	PS(b,c)			
Benzo(b)fluoranthene + Benzo(k)fluoranthene	PAH	10	460	PS(b,c)			
Anthracene	PAH	9	102	PS(b)			
Phenanthrene	PAH	4	68	RBSP			
Contamination	mainly from	urban settlements (sect	ion 3.5)				
DEHP	Plasticiser	11	101	PS(b)			
4-Nonylphenol	Surfactant	8	184	PS(b)			
polybrominated diphenylethers	Flame retardants	7	23 320	PS(b,c)			
Contamination	from metals	- mining and use (section	on 3.6 ^d)				
Cadmium	Metal	19	991	PS(b)			
Nickel	Metal	18	600	PS			
Lead	Metal	17	413	PS			
Zinc	Metal	18	1 454	RBSP			
Copper	Metal	16	808	RBSP			
Arsenic	Metalloid	13	385	RBSP			
Chromium	Metal	10	110	RBSP			
Cyanide (total + free)	lon	8	72	RBSP			
Contamina	tion mainly fro	om agriculture (section	3.7)				
Hexachlorocyclohexane	Insecticide	10	104	PS(b)			
Isoproturon	Herbicide	7	198	PS			
MCPA	Herbicide	6	159	RBSP			
Metolachlor	Herbicide	5	115	RBSP			
Terbuthylazine	Herbicide	6	51	RBSP			
2-4 D (2,4-Dichlorophenoxyacetic acid)	Herbicide	4	18	RBSP			
Malathion	Insecticide	4	13	RBSP			
Parathion	Insecticide	4	7	RBSP			
Contamination mainly from navigation (section 3.8)							
Tributyltin-cation	Biocide	14	659	PS(b,c)			

Notes:

For explanation of criteria and structure of table see text.

Source: WISE-Freshwater WFD accessed 20 August 2018. Data from "EU 25" ie 25 Member States (EU-28 except Greece, Ireland and Lithuania). Priority Substances:

 $\frac{https://tableau.discomap.eea.europa.eu/t/Wateronline/views/WISE_SOW_FailingRBSP/SWB_FailingRBSP_Europe?:embed=y\&:display_count=no\&:showVizHome=no$ ecological status moderate, poor and bad

- (a) under the WFD EU-wide standards apply for priority substances (PS), while national or river basin standards apply for River Basin Specific Pollutants (RBSP).
- (b) defined as priority hazardous substances, for which all discharges, emissions and losses must be ceased.
- (c) Substance is ubiquitous, persistent, bioaccumulative and toxic (uPBT) as defined in 2013/39/EU.
- (d) Another 6 chemical elements exceeded standards for RBSP in at least four Member States (Barium, Selenium, Boron, Cobalt, Uranium, Thallium) plus PCBs.

It can be seen from Table 3.1 that chemicals causing most failures of chemical status are mercury and polybrominated diphenylethers (pBDEs). Other substances causing failure do so in much lower numbers of water bodies.

Legacy pollutants

One of the challenges in status assessment is that some chemicals can be present in the aquatic environment a long time after they were originally discharged or emitted. This "persistence" means that even after effective measures have been put in place to prevent pollution, the chemical can still cause poor water quality, because some chemicals do not break down and are instead recycled through sediments, water and organisms. Typical situations are mining districts and those areas which received industrial effluents from when there was little regulation (Box 3.3). In the case of mercury, there is now much regulation to prevent losses, but historic and natural sources (volcanoes) lead to widespread pollution in central and northern Europe, though continued coal burning represents a current source.

3.3. Emission sources and pathways

Having identified the substances causing poor water quality, the WFD requires investigation of the pressures causing that. In the reporting of 2nd RBMPs there is not a direct link between a substance failing in a water body and the pressure(s) causing that. Instead, we looked at reporting under the EPRTR, the WFD inventory of emissions, discharges and losses of priority substances and WISE-State of Environment reporting https://www.eea.europa.eu/data-and-maps/data/waterbase-emissions-5. The aim was to identify trends in chemical discharges, given the difficulty of disentangling historic pollution from current, so as to see whether emissions are increasing or decreasing.

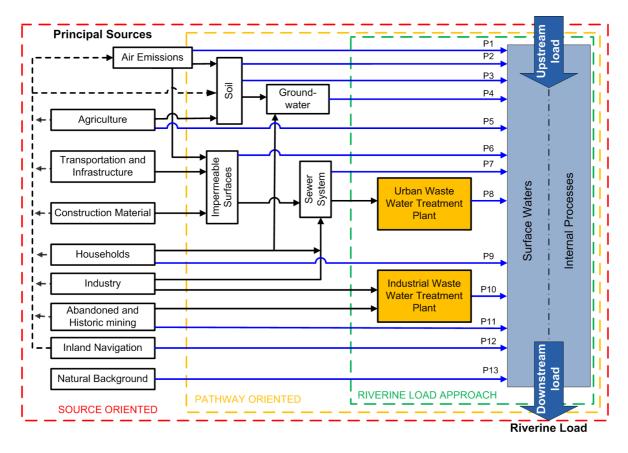
There are different approaches to recording emissions. One looks at the emissions from a known source – e.g. a manufacturing or waste water treatment plant. This "source-oriented" approach addresses the whole system, starting from the principal sources of substance release. The E-PRTR is an example of this, where emissions of particular chemicals above a certain amount per year must be reported by the operator. Pathways are the routes by which substances can be transported to the aquatic environment, with the "pathway-oriented" approach modelling where pollutants may be temporarily stored (e.g. in soils) before eventually reaching surface waters through other processes e.g. erosion or storm water overflows. The "riverine load oriented approach" estimates the observed total load in the river and can include an estimate of the diffuse inputs. Riverine loads describe the mass of the pollutant transported in the river. Both the WFD inventory and WISE SoE emissions reporting allow reporting under

each of these three approaches. While accommodating different approaches, these diverse methods can make it difficult to compare results.

Both point source – from a known discharge – and diffuse source – from multiple sources in an area - should be covered by emissions reporting. In practice, reporting from point sources is generally more straightforward, dominating emissions reports.

A general scheme setting out principal sources, pathways and intermediates has been developed under the WFD for the Inventory of emissions, discharges and losses of priority substances, shown in Figure 3.1 (EC, 2012).

Figure 3.1 Relationship between the different surface water compartments and pathways (P1-P13) (EC, 2012)



P1	Atmospheric Deposition directly to surface water
P2	Erosion
P3	Surface runoff from unsealed areas
P4	Interflow, Tile Drainage and Groundwater
P5	Direct discharges and drifting
P6	Surface Runoff from sealed Areas
P7	Storm Water Outlets and Combined Sewer overflows + unconnected sewers
P8	Urban Waste Water treated
P9	Individual - treated and untreated- household discharges
P10	Industrial Waste Water treated
P11	Direct Discharges from Mining
P12	Direct Discharges from Navigation

Figure 3.1 provides a way to compare emissions reported under the different approaches. On the left, the principal sources of the pollutants are shown, representing groups of sources. Emissions, discharges or loads can follow different pathways, either directly to surface water, or to other compartments of the environment (air, soil, groundwater), represented by the middle section of the Figure. Emissions can be the result of losses during the production or as a result of the use of products. A part of the wastewater from industry and households is collected in a sewer system and treated in industrial waste water plants (P10) or urban waste water treatment plants (P8) (UWWTPs), on the right hand side of the Figure.

In this chapter, main pathways are considered but substances have more ways of entering the aquatic environment.

Emissions datasets provided in Figures 3.2 to 3.14 (tables A1 to A9 in Annex A).

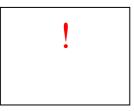
- E-PRTR are data from large sources, either industry or urban waste water treatment plants serving over 100,000 people (or equivalent). Data have been reported under this EU obligation since 2007.
- WFD is reporting of the emissions inventory for each river basin district, required for priority substances for the first time in the 2nd RBMPs, for the year 2010.
- WISE reporting is voluntary reporting of emissions by EEA's member countries.
- "Estimated diffuse 2010" are those from a project calculating diffuse loads to surface water (Roovaart et al (2013a, 2013b)

The WFD inventory should contain information on priority substances. Emissions data below therefore focus on emissions reporting of priority substances, though more information is available on RBSPs (https://www.eea.europa.eu/themes/industry/industrial-pollution/; Roovaart et al, 2017).

What should the emissions data tell us?

In the tables, the lowest emissions estimate would be expected to be the E-PRTR, as these reports include emissions from large installations only. We would expect WISE SoE data to be the same or higher as E-PRTR. WFD data, which should include all the losses, emissions and discharges ought to be higher than E-PRTR. However, this is often not the case and it is unclear which are the most accurate values.

The WFD inventory reporting was expected to provide data on emissions of priority substances into each river basin. Study of the emissions therefore focused on the priority substances identified as key pollutants in Table 3.1. However, owing to the limited reporting, and poorly comparable data, rather little information can be gleaned from the WFD emissions inventory.



Specific details on the emissions datasets can be found in Annex A.

3.4. Contamination through atmospheric deposition

EEA's RBMP Assessment (2018) showed that atmospheric deposition was the major source of contamination of Europe's surface waters.

Table 3.1a: List of pollutants most frequently exceeding EQS in EU25

Pollutant	Type / Use of chemical	No of Member States with EQS exceedance	No. of WBs exceeding (a)	Priority substance (PS) / RBSP (a)
Contaminati	on mainly thro	ough atmospheric depos	sition	
Mercury	Metal	22	45 739	PS(b,c)
Benzo(g,h,i)perylene + Indeno(1,2,3-cd)-pyrene	PAH	13	3 080	PS(b,c)
Fluoranthene	PAH	13	1 324	PS
Benzo(a)pyrene	PAH	11	1 627	PS(b,c)
Benzo(b)fluoranthene + Benzo(k)fluoranthene	PAH	10	460	PS(b,c)
Anthracene	PAH	9	102	PS(b)
Phenanthrene	PAH	4	68	RBSP

⁽a) under the WFD EU-wide standards apply for priority substances (PS), while national or river basin standards apply for River Basin Specific Pollutants (RBSP).

3.4.1. Mercury and its compounds

Sources and uses

Mercury is a natural substance. It can enter the environment from coal burning and industrial processes such as in the chlor-alkali process for commodity chemicals, cement manufacture and in small-scale gold mining. It is also released during volcanic eruptions. Mercury has had many historical uses which have since been phased out (e.g. thermometers, dental amalgam, hat making). It has no known essential function for living organisms.

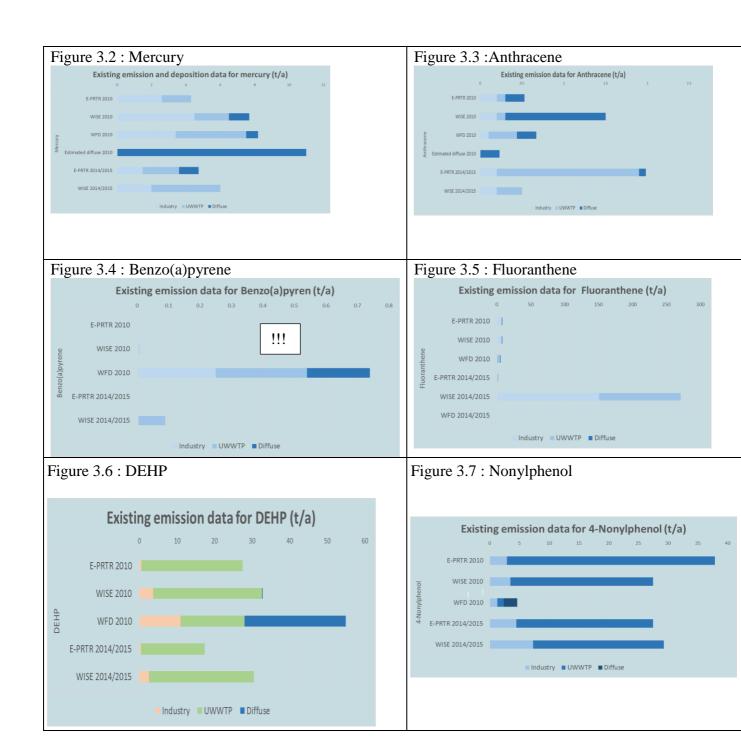
Toxicity and EQS

Mercury and its compounds are toxic and can accumulate in the food chain. Microbial methylation can occur in water, converting inorganic mercury to more toxic organo-mercury compounds. Methylation can also occur in organic environments like organisms and in humic substances, and is thought to be one of the reasons that "unpolluted" areas like Scandinavia show high mercury content in biota (Pirrone et al., 2010).

The EQS is derived to protect predators such as sea eagles or otters from secondary poisoning through eating contaminated fish. In particular, it protects against methyl mercury, which accumulates in the food chain. Fish consumption can be an important source of mercury to humans, where fish plays a significant role in the diet.

⁽b) defined as priority hazardous substances, for which all discharges, emissions and losses must be ceased.

⁽c) Substance is ubiquitous, persistent, bioaccumulative and toxic (uPBT) as defined in 2013/39/EU.



Notes: !!! – CAUTION – low confidence in data, as limited reporting of this substance, see Table 3.2. Details on the emissions data are given in Annex A. Loads given in these figures cannot be summed, as there may be double counting.

WFD status

Mercury and its compounds are ubiquitous priority hazardous substances, and caused failures to achieve good chemical status in nearly all Member States, to a total of 41 % of Europe's surface water bodies. Despite it being a well-characterised, historic pollutant, there was widespread variation in the degree to which mercury did not meet the EQS – from 1-100% surface water bodies.

If comparing results between countries, it should be noted that there were different approaches towards monitoring and reporting of mercury for the second RBMPs. Member States could monitor in water, sediment and/or biota, and there were different approaches towards interpreting the data. Some countries extrapolated failure to meet the standard at monitoring sites to all water bodies, while others reported failure only where failure was confirmed (EEA, 2018a). Typically, measurements of mercury in biota extrapolated to all similar water bodies lead to widespread failure to meet the EQS.

Emissions

The concentrations of mercury in water depend on geology, historical pollution in sediments, concentrations in precipitation and industrial emissions. Mercury can enter surface waters through direct emissions, such as from urban waste water treatment plants and industry. As it is readily released as a vapour, it can be widely-distributed through atmospheric deposition in dust and rain.

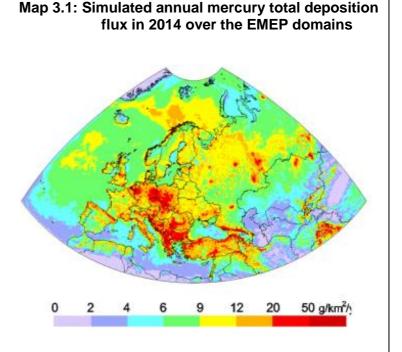
Figure 3.2 summarises data available for mercury emissions to water for Europe. Many countries report mercury emissions, giving confidence in the data. For 2015, a conservative total of mercury to European surface waters is estimated at being 2 t from industry, 4 t from urban waste water treatment plants (UWWTPs), and 2.5 t direct deposition from the atmosphere.

Emissions from UWWTPs are known to be under-reported (Roovaart et al., 2013b). In 2010, these missing emissions were estimated as being 8.4 t. Data reported under WISE for 2014-2015 indicate atmospheric deposition as an important pathway, corroborating the information provided under WFD. Modelled atmospheric deposition of approximately 44 t deposition on the whole EU area (land and surface water) modelled by EMEP (EMEP, 2017) (Box 3.1). A significant part of this 44 t will end up in the surface water via the pathways erosion and run off from paved surfaces.

Box 3.1: Modelling atmospheric emissions of mercury

Modelled data for emissions of mercury to air go back further in time than direct emissions, providing more information on trend over time. According to modelled emissions to air (EMEP, 2017) the trend in Europe is declining from 109 ton in 2005 to 63 ton in 2015. In map 2.1, the deposition of anthropogenic emissions in 2013 is shown (EMEP, 2017). In Europe, the derived anthropogenic mercury deposition is almost equally from European and foreign emissions.

MSC-E, 2016, http://www.msceast.org/index.php/pollution-assessment/and-more



Summary/outlook

That mercury emissions have in decreased over recent decades is unlikely to result in an improvement in chemical status of surface water bodies. Mercury will continue to be recycled between water, sediments and biota. Meanwhile, mercury which is transported to marine waters concentrates in top predators such as tuna and shark, leading to advisory restrictions on human dietary intake.

Atmospheric deposition is an important source of mercury to European surface waters, but it is not the only one and not the largest. Loads from atmospheric deposition and from industry are declining as a result of action to reduce emissions. However, further effort to reduce emissions of mercury from urban waste water treatment plants, either upstream or before discharge, seems necessary.

3.4.2. Polycyclic aromatic hydrocarbons (PAHs)

Sources and uses

PAHs are a natural component of coal and oil, historically being used in wood preservatives and tar products. They are mainly formed by incomplete combustion of organic material, such as coal, petrol and wood, and are commonly released into the atmosphere as small particulates (Abdel-Shafy and Mansour, 2016). Sources to the European environment now include vehicle exhausts, coal-fired power generation, domestic heating and forest fires.

Toxicity and EQS

The PAH substance group comprises a large number of substances, with different toxicities and environmental fates (EC, 2011a). EQS have been set for seven of the most toxic PAH, as

representatives of the whole group. Two of these are separately listed (anthracene and fluroanthene) while the other five are grouped, with the "lead substance" being benzo(a)pyrene. PAHs cause cancer (e.g. they are present in cigarette smoke). The EQS is set to protect humans, who are the most sensitive species through consumption of fishery products.

WFD status

PAHs cause failures to achieve good chemical status in 100s-1000s surface water bodies (table 3.2), across 9-13 Member States. There is however some skewing of the results – over 1000 water bodies failed for benzo(a)pyrene in Germany and for benzo(g,h,i)perylene + Indeno(1,2,3-cd)-pyrene in France.

Emissions

For most PAHs, only a limited number of countries report emissions from industry and UWWTPs. There is more reporting of fluoranthene and anthracene, but still from fewer than half of European countries. This limited reporting means that trends can be skewed by one-off reporting of high loads¹¹.

Figures 3.3-3.5 give an overview of the different reported loads for anthracene, benzo(a)pyrene and fluoranthene. For all PAHs, industry and UWWTPs seem to be significant sources. Atmospheric deposition directly to surface water is the largest reported pathway, taking into account the small number of countries that report.

An overview of the total emissions to water in Europe cannot be given for the PAHs. The data appear to be too inconsistent to assess any trends, owing to the limited number of countries reporting and inconsistent reporting between datasets.

Emissions to air have fallen substantially since 1990 (EEA, 2018c). The main sources to air are now from industry and domestic use.

Summary/Outlook

As atmospheric pollutants with multiple sources arising from the burning of organic matter, reducing the pollution of water bodies by PAHs will remain challenging. A shift to electric vehicles could reduce some diffuse sources, while that from domestic heating (as wood or coal) requires sustained and significant effort.

The low level of reporting of emissions of well-characterised pollutants such as PAHs is disappointing. There is a need for improved understanding of pressures from emissions reporting to be able to implement effective measures to reduce pollution of water by PAHs.

3.5. Contamination from urban settlements

EEA's RBMP Assessment showed that contamination from urban waste water treatment was the major point source of contamination of Europe's surface waters. Note that in most cases

¹¹ WISE 2014/2015 Fluoranthene, Industry: 150 t by one country, 0.7 t by 12 other countries; WISE 2014/2015 Fluoranthene, UWWTP: 120 t by two countries, 0.2 t by 5 other countries.

treatment plants are recipients of contaminants from upstream uses and discharges, providing a known pathway into the aquatic environment, rather than they themselves being the user of hazardous substances.

Table 3.1b: List of pollutants most frequently exceeding EQS in EU25

Pollutant	Type / Use of chemical	No of Member States with EQS exceedance	No. of WBs exceeding (a)	Priority substance (PS) / RBSP (a)
Contar	nination mainly	from urban settlements	S	
DEHP	Plasticiser	11	101	PS(b)
4-Nonylphenol	Surfactant	8	184	PS(b)
Brominated diphenylethers	Flame retardants	7	23 320	PS(b,c)

⁽a) under the WFD EU-wide standards apply for priority substances (PS), while national or river basin standards apply for River Basin Specific Pollutants (RBSP).

3.5.1. **Bis(2-ethylhexyl) phthalate (DEHP)**

Sources and uses

DEHP is a widely-used phthalate, for example as a plasticizer in the manufacture of PVC. It has other uses, such as in hydraulic fluid, as a dielectric fluid in capacitors, sealing compounds in buildings and an additive in paints, cosmetics and biocides. Although its use is being phased out under REACH, DEHP's widespread use in e.g. plastic water pipes represents a potential source to the environment for many years to come, owing to the long lifetime of those products.

Toxicity and EQS

DEHP is persistent in sediments and soils, but does not bioaccumulate in organisms. The main harmful effect is endocrine disruption to aquatic organisms, adversely affecting reproduction and growth.

WFD status

Despite its widespread use, DEHP caused failures in relatively few water bodies (table 3.1). This may be because it is relatively well removed by conventional waste water treatment, concentrating into the sludge (Gardner et al, 2014).

Emissions

Figure 3.6 gives an overview of the different reported loads.

About half the Member States, plus Norway, reported DEHP loads from industry and UWWTPs, showing that UWWTPs represent the most significant point source. There is a declining trend in reported loads from industry, while trends from UWWTPs are harder to assess owing to large fluctuations in some reported loads. Emissions of diffuse sources are difficult to compare owing to different approaches used by different countries and low levels of reporting. Important diffuse sources seem to be stormwater overflows and households not connected to the sewerage system.

Summary/Outlook

⁽b) defined as priority hazardous substances, for which all discharges, emissions and losses must be ceased.

⁽c) Substance is ubiquitous, persistent, bioaccumulative and toxic (uPBT) as defined in 2013/39/EU.

The major source of DEHP appears to be from UWWTPs, though diffuse sources may also be significant (Fig 3.6). Over time, the replacement of DEHP in plastics should lower the concentrations of DEHP reaching UWWTPs.

While it is hard to assess trends from the existing data, the decades-long lifetime of products containing DEHP would suggest that chemical status is unlikely to change much without significant effort to reduce emissions from the UWWTPs, whether that is at the plant itself or by preventing discharges into the sewerage system, e.g. through waste controls.

3.5.2. Nonylphenol

Sources and uses

Nonylphenol is a precursor in the production of nonylphenol ethoxylates (NPE), used in manufacturing as antioxidants, lubricating oil additives, emulsifiers and as solvents. It acts as a surfactant, such as in wetting agents or detergents, and can be found in paints, pesticides, imported textiles and personal care products. Where NPE was used in clothes, much of it seemed to enter the sewerage system following washing in domestic washing machines (Environment Agency, 2013).

In urban waste water treatment, nonylphenol ethoxylates break down to nonylphenol.

Toxicity and EQS

Nonylphenol is toxic for aquatic organisms, particularly for algae and invertebrates (CIRCABC, 2005). It has endocrine-disrupting effects particularly on fish.

WFD status

Nonylphenol was reported as causing failure to achieve good chemical status in 8 Member States, mainly in western Europe. Half the failures were reported as being in France.

Emissions

Figure 3.7 gives an overview of the different reported loads.

About half the Member States, plus Norway, reported loads from industry and UWWTPs. Trends for industry seem to be increasing, but those for UWWTPs seem to be decreasing. A few Member States reported diffuse sources for the WFD inventory, suggesting that unconnected households, stormwater overflows and run-off were the main pressure, but limited reporting makes assessment difficult.

Overall, it is difficult to be confident in the emissions data for nonylphenol, because extreme differences between Member States suggest different approaches to monitoring or quantification.

Summary/Outlook

Restrictions on the use of nonylphenol and NPE should lead to a decline in emissions to water. Nonylphenol is not persistent (Mao et al, 2012) so it should cause fewer failures to achieving good chemical status in surface waters in future.

3.5.3. Brominated diphenylethers (pBDEs)

Sources and uses

Polybrominated diphenylethers (pBDEs) are a group of 209 substances which have been used in many products as flame retardants. They have been used, for example, in electronics, furniture and textiles (EPA, 2017).

Toxicity and EQS

pBDEs are ubiquitous in the environment and some are restricted under the Stockholm Convention owing to their widespread use, very persistent and bioaccumulative properties. A group of 6 representative pBDEs is regulated under the WFD¹². The EQS is set to protect human health from pBDEs consumed in fishery products.

WFD status

The EQS for pBDEs was exceeded in 21% of surface water bodies. Seven Member States reported failures to achieve good chemical status for pBDEs, the vast majority of which were in Sweden (23 185 water bodies of the total 23 320 not meeting the EQS) (see Table 3.1).

Emissions

Figure 3.8 gives an overview of the different reported loads.

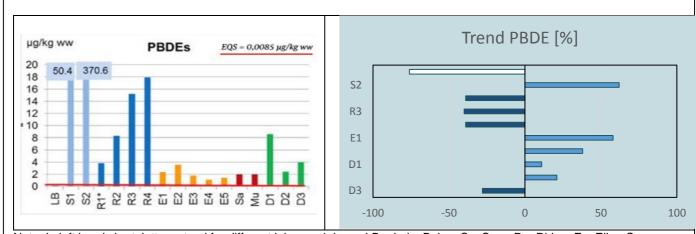
There is very little reporting of emissions of pBDEs. The few Member States reporting to the WFD inventory show highest loads from industry, followed by diffuse sources and UWWTP. The few reported diffuse loads suggest atmospheric deposition and households may be relevant sources. In consequence, it is difficult to offer anything quantitative about total emissions to water in Europe, or to discuss trends. Studies can offer some insight (Box 3.2)

¹² For the group of priority substances covered by brominated diphenylethers, the EQS refers to the sum of the concentrations of congener numbers 28, 47, 99, 100, 153 and 154. Four of them: Tetra, Penta, Hexa and Heptabromodiphenylether (CAS -numbers 40088-47-9, 32534-81-9, 36483-60-0, 68928-80-3, respectively) are regulated as priority hazardous substances.

Box 3.2 - pBDEs in fish in German rivers

Germany shows widespread and very high exceedance of the EQS (shown by red line) in fig. B3.2, left. Trends between 1995 and 2013 vary between different rivers. The Rhine shows decreasing concentrations, while concentrations in other rivers are mostly increasing.

Fig. B3.2: Brominated diphenylethers in fish of the German Environmental Specimen Bank (left: concentrations 2013; right: trends Year 1995 – Year 2013)



Note: In left hand chart, letters stand for different lakes and rivers: LB – Lake Belau, S – Saar, R – Rhine, E – Elbe, Sa – Saale, Mu – Mulde, D – Danube. The red line just above horizontal axis shows the EQS of 0.0085 ug/kg. In the right hand chart, dark bars show trend of decreasing concentrations of pBDEs in fish, blue bars show increasing trend in concentrations.

Source: Fliedner et al. 2016

In contrast to many substances used historically, such as mercury, pBDEs began to be widely used as flame retardants only in the early 1990s. Environmental concerns began to be identified within a few years, with a Directive setting out restriction on use of pentaBDE and octaBDE in 2003 (EC, 2003). In 2008, PBDEs were included in the list of priority hazardous substances under the EQS Directive and in 2009, pentaBDE and octaBDE were listed under the Stockholm Convention (section 1.3). The European Food Safety Agency issued scientific opinions on brominated flame retardants in the food chain 2010-12. Thus regulatory action began relatively rapidly, reflecting the improved understanding of harmful chemicals in the environment and legislative means to act.

Such emissions and pressures information as are reported by countries available suggest that it is not clear how pBDEs are reaching the aquatic environment. The widespread contamination reported by Sweden was attributed to atmospheric deposition. Pathways to soil and water, through waste disposal and washing (which allows pBDEs to enter the sewers and hence UWWTPs) show that most of the pBDEs bind to solid matter (Anderson and MacRae, 2006; North, 2004; Zhang, et al, 2017). Other researchers report a significant atmospheric transport role (Ricklund et al, 2010; Earnshaw, et al, 2013) though brominated flame retardants were not associated with emissions of soot or small particles (Egeback et al, 2012).

Summary/Outlook

One of the striking features about pBDEs is the apparent mis-match between WFD status and emissions reporting. Most Member States reported no emissions of pBDEs under E-PRTR or WISE, with only four Member States reporting some under the WFD inventory.

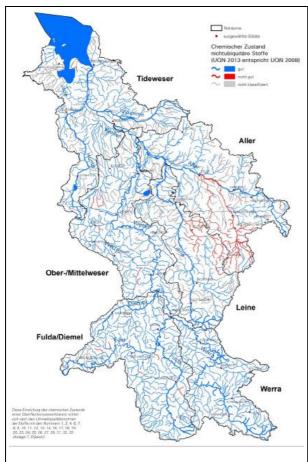
While the large number of surface water bodies failing for pBDEs can currently be attributed to Sweden, it seems likely that more Member States will report failing chemical status for them in future. This is because of a change in the way in which the EQS is to be measured (from water to concentrations in biota). In the 2nd RBMPs, Sweden applied this new EQS to its chemical status assessment: in future, so will other countries. Although many pBDEs have now been restricted, owing to their chemical behaviour and persistence, it seems likely that they will continue to cycle between biota and sediments for many years.

It is not clear that we fully understand the major transport pathways for pBDEs into the aquatic environment. There is a need to better understand the environmental pathways of pBDEs, to identify whether measures can be implemented which would limit further dispersal.

3.6. Contamination from metals - mining and use

Metals have been used for centuries in many different applications. As well as leading to high concentrations in naturally metalliferous areas, their extraction and processing have led to polluted districts - even long after mines have closed down (Box 3.3). Widespread use of metals in industry, and subsequent discharge to water also continues to cause pollution, as metals are transported within the water column and its sediments.

Box 3.3: Ancient Mining in the Harz Mountains in Germany



Metals e.g. lead and cadmium exceed the EQS in the Harz Mountains foothills of Weser River in northern Germany. For centuries, it was one of important ore mining regions of Germany. The mining activity mainly closed down in the 1930s and in 1992 the last mine closed. Around the mines are a large number of tips and chemical and metallurgic industry. The rivers most contaminated are some tributaries of the Leine River, which has a catchment area of about 6.500 km². Metal contamination down the river is visible until the estuary of the Weser in the North Sea.

The river and floodplain sediments have been contaminated with the waste and mine water over centuries. In the floodplains high lead and cadmium concentrations affect the agriculture at pasture and arable land along the river floodplains. Livestock farming and agriculture is possible in limited form only. [Owing to the large area affected,] decontamination would be very difficult and lowering concentrations of the metals in the rivers represents a long term effort (FGG Weser, 2016). Similar contamination and effects on waters are seen all over Europe in old mining regions.

Map 3.2, Metal pollution from mining areas in the Harz catchment.

Source: http://www.fgg-weser.de/component/jdownloads/send/8-eg-wrrl/331-bwp2015-weser-final-textteil-160318

Table 3.1c: List of pollutants most frequently exceeding EQS in EU25

Pollutant	Type / Use of chemical No of Member States with EQS exceedance		No. of WBs exceeding (a)	Priority substance (PS) / RBSP (a)
Contami	ination from n	netals - mining and use	1	
Cadmium	Metal	19	991	PS(b)
Nickel	Metal	18	600	PS
Lead	Metal	17	413	PS
Zinc	Metal	19	1503	RBSP
Copper	Metal	16	845	RBSP
Arsenic	Metalloid	14	397	RBSP
Chromium	Metal	10	110	RBSP
Cyanide	lon	8	74	RBSP

⁽a) under the WFD EU-wide standards apply for priority substances (PS), while national or river basin standards apply for River Basin Specific Pollutants (RBSP).

Sources and uses

Metals are natural substances and have been mined for centuries and used in many different ways, from producing tools, vehicles and buildings to sophisticated applications in industrial processes, as well as numerous domestic applications. Some historic uses shown to be particularly harmful, and so restricted, include the use of lead in water pipes and as a petrol additive. (Mercury is discussed in section 3.4.)

Metals reach the aquatic environment in many ways, reflecting their multiple uses. Rainfall may leach them from mines, industrial or waste sites, they may be discharged in effluents to sewers or directly into rivers, lakes, etc. Being natural elements, metals do not degrade, although they can be converted to other forms which may be more or less harmful. Many dissolved metals can bind to suspended material and sediment and be transported downstream, or recycled within a water body.

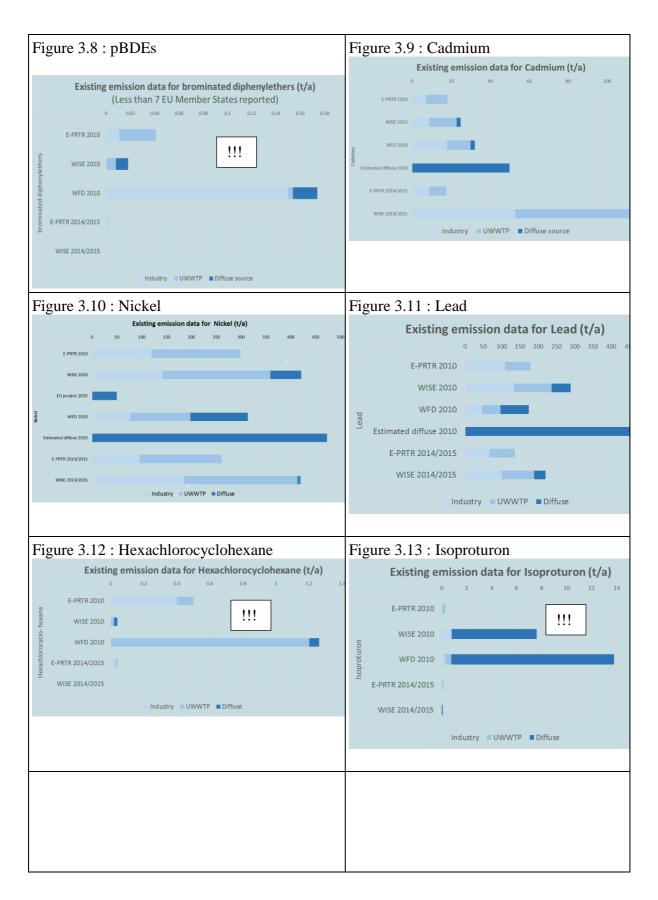
Toxicity and EQS

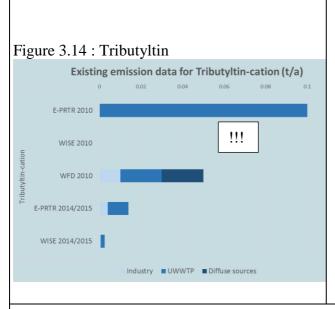
Since metals occur naturally in the environment and some metals are essential elements for living beings, it is not always easy to assess when concentrations start having negative or even toxic effects. These can vary for individual species and the environment conditions.

The solubility and bioavailability of metals are influenced by pH, organic compounds naturally present in water (such as humic substances) and calcium. Ecotoxicological effects are exacerbated in soft water (i.e. low lime content) and low pH. Increasing knowledge about the detrimental impacts of metals have led to extensive monitoring and research into the ecotoxicological effects. Modelling of metals under such differing conditions has been undertaken to assess their bioavailability, allowing assessment of measured concentrations with the bioavailable concentration. This can be used to target measures where the metals present most risk to aquatic organisms. The 2013 Priority Substances Directive included bioavailable EQS for nickel and lead.

⁽b) defined as priority hazardous substances, for which all discharges, emissions and losses must be ceased.

The EQS for cadmium and lead are set to protect invertebrates, while that for nickel is set to protect algae and molluscs.





Notes: !!! – CAUTION – low confidence in data, as limited reporting of this substance, see Table 3.2. Details on the emissions data are given in Annex A.

Loads given in these figures cannot be summed, as there may be double counting.

WFD status

Among the 15 priority substances most frequently causing failure to achieve good chemical status are the metals mercury (discussed in section 3.4), cadmium, lead and nickel. This may reflect a relatively high level of reporting for metals, with approximately 2/3 Member States reporting failures to achieve chemical status for these substances. An additional five metals – zinc, copper, arsenic, chromium and cobalt - are among the most frequently-reported RBSPs causing failure of ecological status. There were more failures in surface water bodies for zinc and copper than for many of the priority substances.

Despite widespread use, failures to achieve good chemical status for cadmium, lead and nickel range from 413-991 (table 2.1) in surface water bodies. Member States are making progress with these metals - 969 water bodies improved from poor to good chemical status from the first RBMPs, though 2288 water bodies were still failing (EEA, 2018a).

Emissions

Figures 3.9-3.11 give an overview of the loads reported under different mechanisms. For other metals, there are limited, comparable, emissions data as the WFD inventory only includes priority substances. Further information on E-PRTR reported emissions of zinc and copper are available at https://www.eea.europa.eu/themes/industry/industrial-pollution/ and in Roovaart et al. (2017).

There is a high level of reporting of metals for emissions from industry and UWWTPs. UWWTPs are the largest known source for cadmium and nickel, while for lead it is industry. However, Roovaart *et al.* (2013) suggested that there was significant under-reporting for emissions from UWWTPs for all three metals. Reflecting the widespread use of metals,

countries reported a range of diffuse sources from agriculture, atmospheric deposition, unconnected households, storm water overflows, transport and run-off.

However, despite high levels of reporting of metals emissions, the overall trend is not clear, with high variability from year to year.

Between 2007 and 2014, arsenic and copper emissions reported under the E-PRTR for industry excluding UWWTPs showed no clear trend, while there was a decrease in zinc emissions (Roovaart et al, 2017). For UWWTPs reporting under E-PRTR, there was a slight increase in copper and zinc emissions, with a large increase in reported arsenic emissions from one country.

Summary/Outlook

Both research into the behaviour of cadmium, lead and nickel in the aquatic environment, and regulation around that, has been undertaken for decades. While there are still a significant number of surface water bodies failing to achieve good chemical status for metals, there are promising signs that further improvements can be made.

Forthcoming challenges may include the behaviour of metals as "co-contaminants", where their presence at low levels may exacerbate the toxicity of other chemicals present in the same water body (chapter 2).

3.7. Contamination from agriculture

The aim of pesticides and biocides is to have a harmful effect at the point of use, protecting crops and ensuring food security. However, owing to direct application into the environment, effects on organisms can occur beyond the intended target.

Data reflecting actual emissions of pesticides are often few, despite widespread use. This partly reflects many diffuse sources, for which reporting is in any case weak, and also owes to the way that water and pesticides legislation affects reporting at the European level (Box 3.4). For this reason, trends in pesticide sales have be taken as a proxy for emissions, though this must be seen as indicative and provides little geographic information.

EU sales statistics were relatively stable between 2011 - 2014, with 360 000 - 400 000 t sold per year (Eurostat, 2018). The group with the highest sales were fungicides and bactericides (about 43%), followed by herbicides (35%) and insecticides (5%).

Table 3.1d	Contamination	on mainly from agricultu	ure	
Hexachlorocyclohexane	Insecticide	10	104	PS(b)
Isoproturon	Herbicide	7	198	PS
MCPA	Herbicide	6	159	RBSP
Metolachlor	Herbicide	5	115	RBSP
Terbuthylazine	Herbicide	6	51	RBSP
2-4 D (2,4-Dichlorophenoxyacetic acid)	Herbicide	4	18	RBSP
Malathion	Insecticide	4	13	RBSP
Parathion	Insecticide	4	7	RBSP

(b) defined as priority hazardous substances, for which all discharges, emissions and losses must be ceased.

This section starts with insecticides, then considers herbicides. Fungicides and bactericides do not appear high up in the lists of most frequently reported pesticides (table 3.1).

3.7.1. **Insecticides**

Eleven Member States reported hexachlorocyclohexane (HCH) exceeding the EQS (table 3.1). Two other insecticides – parathion and malathion, regulated as RBSPs – were reported by four Member States. Otherwise no other insecticides were reported as causing failure in four or more Member States.

Hexachlorocyclohexane

Sources and uses

In the priority substances list, HCH represents a group of several, similar molecules. Lindane – gamma-HCH - is the most well-known substance in the group. It was extensively produced in the EU from the 1950s, and used as a broad-spectrum insecticide until the 1970s - 1990s. Production led to large amounts of HCH-contaminated waste. Production sites were located near rivers and so there are many HCH contaminated spots beside rivers (i.e. Sabiñánigo and Vitoria sites next to the Ebro river).

Hexachlorocyclohexane is relatively long-lived in the environment, is highly volatile and can be transported over long distances through natural processes. It has been listed under the Stockholm Convention since 2009.

Toxicity and EQS

HCH is carcinogenic, persistent, toxic and can bio-accumulate in food chains. The aim of the EQS is to protect top predators such as otters and cormorants, which are at risk owing to bioaccumulation.

WFD status

Despite restrictions on use for several years, HCH caused failures in 10 countries and over 100 surface water bodies. This reflects the persistence of the substance and some continued use. However, despite its volatility, in contrast to mercury it is not reported as causing many failures in northern countries.

Emissions

Figure 3.12 gives an overview of the different reported loads. Few Member States report loads of HCH from industry and UWWTPs, and there is inconsistency between reports. Those reported under E-PRTR suggest a decreasing trend, but are skewed by high loads in the chemical industry and energy sector reported by a single country, even though many uses have been restricted. There was very limited reporting on diffuse sources like atmospheric deposition and stormwater overflows.

No overview of the total emissions to water in Europe can be made, because only a few Member States have reported emissions. It is unclear whether this arises because of low emissions or because of low levels of reporting.

Summary/Outlook

Restrictions on the use of HCH suggest that over time, failures to achieve good chemical status owing to this insecticide should decrease.

Parathion and malathion

Both parathion and malathion are organophosphorus-compounds and inhibit acetylcholine esterase (AChE; further description in table 2.1). Studies with the plankton, Daphnia, showed that long term exposure to low concentrations was harmful (UBA, 2011).

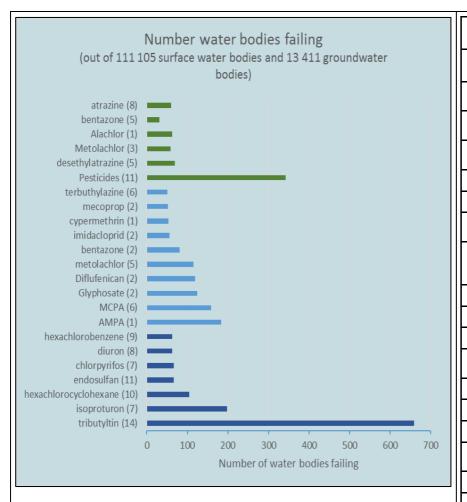
Parathion and marathion are regulated as RBSP by several Member States and exceeded EQS in only a few water bodies.

No reliable figures on emissions of parathion and malathion are available.

Box 4.4: Where are the pesticides in 2^{nd} RBMPs?

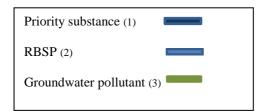
Pesticides do not appear as a significant cause for failure to achieve good (chemical) status of water bodies, despite expert views that pesticides – substances designed to eliminate part of an ecosystem - should be of concern. Why don't we see this in the data?

Fig B3.4 shows numbers of water bodies where pesticides cause failure to achieve good status, in surface and groundwaters



Pesticide	Restriction (in 2018) ⁴
tributyltin	Not approved ⁵
isoproturon	Not approved
hexachlorocyclohexane	Not approved
endosulfan	Not approved
chlorpyrifos	Approved
diuron	Approved
hexachlorobenzene	Not approved
AMPA	Glyphosate breakdown product
MCPA	Approved
Glyphosate	Approved
Diflufenican	Approved
metolachlor	Not approved
bentazone	Approved
imidacloprid	Approved ⁶
cypermethrin	Approved
mecoprop	Not approved
terbuthylazine	Approved
Pesticides ⁷	
desethylatrazine	Atrazine breakdown product
Metolachlor	Not approved
Alachlor	Not approved
bentazone	Approved
atrazine	Not approved

Numbers in parentheses are the number of Member States reporting failures owing to that substance.



Why do we see this? Possibly because...

- Restrictions and changed practice have been enacted on many of the substances measured, these controls have been effective and releases to water are reduced;
- Restrictions mean that the monitored substances do not reflect the pesticides actually in use, so the monitoring misses important information;
- Monitoring frequency (typically up to 12 times per year) misses the limited period for which a pesticide is typically in use:
- WFD monitoring takes place in larger waterbodies, rather than small streams;
- Averaging concentrations over the year means threshold standards for chronic exposure are not exceeded;
- Differences in uses of pesticides across the EU mean that for any particular pesticide, there are relatively few records, which means that apparent significance at EU-scale is smaller than for other substances.
- National EQS or threshold values vary so difficult to get comparable picture.

From the RBMP assessments, we could conclude:

Reporting is correct – concerns about pesticides are over-stated. Measures have been effective.

Reporting is correct on reported substances, but we lack information on many other pesticides.

Reporting of status is inaccurate, owing to monitoring not reflecting situation during peak periods of pesticide use.

But, from the reporting, we cannot be sure which of these apply.

Notes

1) Shown are where at least 50 surface water bodies failing for pesticide

https://tableau.discomap.eea.europa.eu/#/site/Wateronline/views/WISE_SOW_PrioritySubstance/SWB_SWPrioritySubstance_Europe?:iid=2

2) Shown are where at least 50 surface water bodies failing for pesticide

https://tableau.discomap.eea.europa.eu/#/site/Wateronline/views/WISE_SOW_FailingRBSP/SWB_FailingRBSP?:iid=1

3) Shown are where at least 25000 km² groundwater bodies failing for pesticide

- 4) EU pesticides database http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN
- 5) Tributyltin is a biocide which was mainly used to combat marine biofouling.
- 6) Imidacloprid is approved but use severely restricted since 2013

 $\underline{\text{https://ec.europa.eu/food/plant/pesticides/approval_active_substances/approval_renewal/neonicotinoids_en}$

7) Active substances in pesticides, including metabolites, where the concentration of any individual exceeds 0.1 ug/l or the sum of total measured exceeds 0.5 ug/l

3.7.2. Herbicides

Isoproturon

Sources and uses

From the 1990s, isoproturon was one of the most commonly-used herbicides in Europe, used to control annual grasses and broad-leaved weeds, for example in cereals. However, because of its toxicity and persistence, approval was withdrawn in 2016 and sales forbidden from March 2017 (EU, 2016).

Toxicity and EQS

The EQS was set to protect sensitive marine species, especially algae (CIRCABC, 2005). Isoproturon is one of several herbicides which affect photosynthesis.

WFD status

Isoproturon was reported as failing in nearly 200 surface water bodies, the majority in western Europe.

Emissions

Figure 3.13 gives an overview of the different reported loads.

Few Member States reported loads from industry and UWWTPs. Loads reported in WFD by two Member States indicate limited loads from industry (presumably related to production), but significant loads from UWWTPs. It is unclear how these arise. Diffuse sources reported by 5 Member States indicate high loads from agriculture and run-off, with minor loads from storm water overflows.

No overview of the total emissions of isoproturon to water in Europe can be made, owing to reporting by only a few Member States. It is unclear whether this arises because of low emissions or because of low levels of reporting.

Summary/Outlook

Restrictions on isoproturon had yet to come into effect in the period during which emissions and water body status information were being collected. As there are limited emissions data available, it seems unlikely that information in future will be able to show any changes. Theory suggests that fewer surface water bodies should fail in the 3rd RBMPs for isoproturon.

Box 3.5: Behaviour of Glyphosate in the environment

Glyphosate

Glyphosate is a commonly-used herbicide which has the highest pesticides sales volume in Germany. It is widely used for killing weeds on fields, public roads, parks and gardens, and glyphosate is often found in waters, crops and humans. Water protection measures to reduce erosion from ploughing – "minimum tillage" - often require the use of a herbicide, which is usually glyphosate.

Glyphosate is designed to kill plants via absorption through the leaves, where it inhibits a plant specific enzyme. When it reaches water, its herbicide action can damage algae and aquatic plants. However, glyphosate breaks down quite quickly in the aquatic environment, over timescales of a few days to a few weeks. Results of water and sediment studies show that, in addition to breakdown by bacteria, a major contributor to the reduction of glyphosate in surface waters is through adsorption to sediment and suspended particulate matter. For these reasons, glyphosate or its breakdown product aminomethylphosphonic acid (AMPA) may be regulated in water.

[pic of tractor spraying – could be in a park]

MCPA, metolachlor, terbuthylazine and 2-4 D

Four other herbicides, regulated as RBSPs, were reported as exceeding their EQS by at least 4 Member States: MCPA, metolachlor, terbuthylazine and 2-4 D.

MCPA is a widely used herbicide, used to control weeds in cereals and other crops. Its main effects in water are upon aquatic plants and algae, inhibiting photosynthesis and carbohydrate production and it can be harmful to fish.

Metolachlor is a pre-emergence herbicide, inhibiting germination of grass species and so allowing crops to grow better. EQS are set to protect algae, as the most sensitive aquatic organisms.

Terbuthylazine is a systemic herbicide, used to control grass and broad-leaved weeds and works as a herbicide by interfering with photosynthesis. The major harmful effect in water is on invertebrates.

2-4 D (2,4-Dichlorophenoxyacetic acid) is a selective herbicide, which effects broad leaved weeds. In water, aquatic plants are the most sensitive organism. (Lewis et al, 2016; UBA, 2011 and 2016)

MCPA and metolachlor both exceeded national EQS in over 100 surface water bodies. Emissions to water data are not available for these RBSPs.

Outlook for pesticides

EU-wide restrictions on use of pesticides should lead to improvements in surface water chemical status for those substances. That we may be seeing that in the data, with relatively few water bodies failing for pesticides, should be understood with caution.

Most pesticides are not regulated under the WFD and so are not reported upon at the EU level. Whole classes of pesticides – fungicides and bactericides – are missing. Substitution of heavily- restricted pesticides, by others which face less scrutiny in the water legislation, means we miss information on many other substances.

3.8. Contamination from navigation

Ships, boats and the infrastructure to support them can cause a range of environmental problems, if poorly managed. For example, dredging channels can disturb buried, contaminated sediments. This section focuses on a contaminant directly introduced into water by shipping activities.

Table 3.1e: Contamination mainly from navigation					
Tributyltin-cation	Biocide	14	659	PS(b,c)	

⁽b) defined as priority hazardous substances, for which all discharges, emissions and losses must be ceased.

Biocide: Tributyltin

Sources and uses

Organisms such as algae and barnacles settle on wood, metal or plastic surfaces a short time after the material has been put in the water. This is a natural colonization process called "fouling" and can degrade the material. On vessels it also slows the boat down, leading to higher energy use. Biocides are therefore used to resist biofouling, which work by coating the vessel's hull with an antifouling coating and continuously leaching the biocide. This also results in water contamination.

Owing to aquatic toxicity and persistence, use of organotin compounds in antifouling coatings has been banned since 2008.

TBT has also been used in wood preservatives, silicone sealants, roof sheeting, textiles and diverse other coatings. The remaining production and use of TBT continues to result in emissions from industry and UWWTPs.

Toxicity and EQS

TBT compounds affect the endocrine (hormone) system of certain marine as well as freshwater molluscs at very low concentrations. This results in malformation of the reproductive system, which can lead to impairment or eventually a complete loss of the ability to reproduce. Severity

⁽c) Substance is ubiquitous, persistent, bioaccumulative and toxic (uPBT) as defined in 2013/39/EU.

of malformation increases with higher TBT concentrations (CIRCABC, 2005). The EQS was derived to protect organisms in both freshwater and saltwater environments.

WFD status

TBT causes failure to achieve good chemical status in surface waters in over 650 water bodies. These are spread across Europe, mainly in western and southern countries. TBT is a uPBT under the WFD, owing to the difficulty in remediating contaminated areas.

Emissions

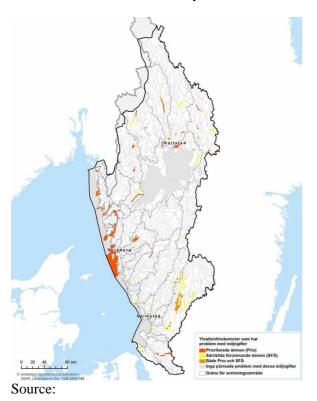
Figure 3.14 gives an overview of the different reported loads.

Few Member States reported loads from industry, UWWTPs and diffuse sources.

No overview of the total emissions to water in Europe can be made, because only a few Member States have reported emissions.

Box 3.6

Map 3.3 Tributyltin (TBT) causing pollution of harbours and leisure navigation areas: Example from Sweden



Despite restrictions, polluted sediments continue to impact on water quality

Shipyards where TBT was used in antifouling coatings for boats led to buildup of TBT in water and sediments over time. One example is the archipelago around Gothenburg and rivers and lakes in the river basin Västerhavet (map 2.2). In the river basin 13 water bodies do not reach the good status due to the exceedance of the TBT EQS. The restriction of TBT-based antifouling coatings stopped the increase of the TBT concentrations in water. But release of TBT from the sediment occurs when sediment is transported in rivers or is dredged to allow access to ports and harbours Vattenmyndigheterna i samverkan. "Del 2, Vattenförvalting 2009-2015 - Resultat Och Samverkan." Länsstyrelsen Västra Götalands län .

http://www.vattenmyndigheterna.se/Sv/publikationer/Pages/default.aspx

Summary/Outlook

Following the restriction on use of TBT in boat antifouling, concentrations of TBT in water and sediments have decreased. Nevertheless, there are still exceedances of the EQS, which may relate to both historic contamination and to uses other than for antifouling.

Other than removing TBT-contaminated sediments and finding safe ways to dispose of hazardous material, there is little that can be done to remediate water bodies failing for this substance. Rather, careful management is required to allow burial of the contaminated material and avoid re-disturbance.

Non-toxic ways to prevent biofouling would have many applications. Finding them would deliver both increased sustainability and market advantage.

3.9. Summary

With the exception of mercury, pBDEs and some of the PAHs, Member States are making significant progress in tackling concentrations of individual priority substances in surface water bodies (EEA, 2018a). This should be seen as a success for European water and chemicals policies stretching back several decades.

Looking deeper, we can see some gaps in the data. Most priority substances have been regulated for many years, with monitoring, analysis and discharge permitting being well-established. It is therefore perhaps surprising that for many of the most frequently-reported priority substances, there is a core set of 8-12 Member States reporting failures of those substances. It is unclear whether this accurately reflects pollution across the EU - that in other countries the priority substances are not a problem - or instead reflects the approach to monitoring and reporting. For instance, at least one country did not report any priority substances as causing failures to achieve good chemical status.

Similarly, at EU level, comparable information on emissions is limited to only a few substances. Table 3.2 gives an overview of the number of Member States reporting for the year 2010 for the different source groups: industry, UWWTPs and diffuse sources. When different datasets are reported (E-PRTR, WISE, WFD), the dataset with the highest number of Member States reporting is shown, i.e. "the best case", summarising the information available on emissions of 15 priority substances. In the table, where emissions data are available for at least 14 countries, the cell is coloured green indicating sufficient data availability. Between 7-14 countries, the cell is yellow, indicating moderate data availability. If data are available for fewer than 7 countries, the cell is red.

Table 3.2: Data availability for emissions of the 15 priority substances most frequently causing failure to achieve good chemical status

Pollutant	Industry	UWWTP	Diffuse sources
Cadmium	24	22	8
Lead	26	22	9
Mercury	22	23	8
Nickel	26	26	9
Anthracene	9	9	7
Benzo(a)pyrene	7	4	5
Benzo(b) fluoranthene	5	2	3
Benzo(k) fluoranhene	5	2	3
Indeno(123cd)-pyrene	5	2	3
Benzo(g,h,i)-perylene	9	7	2
Fluoranthene	14	11	6
4-Nonylphenol	11	16	5
DEHP	14	17	5
Brominated diphenylethers	3	3	4
Tributyltin-cation	5	3	2
isoproturon	7	3	5
Hexachlorocyclohexane	6	4	3

14 or more MS reporting	>= 14
between 7 and 14 MS reporting	14<>=7
less then 7 MS reporting	< 7

It can be seen that there is rather limited emissions information available at European level, even for well-established pollutants like priority substances from point sources. Information on emissions from diffuse sources is poor: as point sources become better controlled, the significance of diffuse sources is getting higher.

These data gaps make it difficult to track progress in reducing emissions at the European level, as required by the WFD, and to assess the effectiveness of chemical source control legislation in protecting the environment.

One of the challenges with chemical status is that once a persistent substance is in the aquatic environment, it may be there for a long time after emissions have ceased. This may lead to continued failure to meet good chemical status, and a potential mis-match with the pressures. In the case of transboundary pollution, there is also a poor fit with the river basin approach promoted by the WFD, which works on the basis that management processes will influence local/regional water quality. In the case of persistent, hazardous chemicals, particularly those which can be transported in the atmosphere, international chemicals legislation is also needed to underpin environmental protection. Evidence on the trend in emissions may be used to better inform the pressures assessment.

Looking forward to the next RBMP reporting, there are some new priority substances and some existing priority substances have revised EQS to reflect updated scientific knowledge. It is likely that these changes will make the achievement of good chemical status in surface waters more challenging.

Specific actions proposed to improve protection of waters.

Further effort to reduce emissions of mercury from urban waste water treatment plants, either upstream or before discharge, seems necessary.

Improved understanding of pressures from emissions reporting needed to be able to implement effective measures to reduce pollution of water by PAHs.

Improved understanding of the environmental pathways of pBDEs, to identify whether measures can be implemented which would limit further dispersal.

Streamlining of emissions reporting, so that robust data collected for one obligation would satisfy European emissions reporting requirements.

Improvement in the monitoring and reporting of diffuse sources, to ensure that pressures are correctly understood and measures can be appropriately targeted.

4. Strategies to reduce chemical pollution of water

4.1. Introduction

A range of legislation exists to protect water from chemical pollution (section 1.3). At EU level, the legislation both:

- protects against pollution in one country being transferred downstream to another; and
- ensures that similar, minimum standards apply in Member States, avoiding unfair competition where weak standards give advantage to polluters compared to others meeting more stringent standards.

The EU's 7th Environment Action Programme (EU, 2013a) mandated the European Commission to develop "a Union strategy for a non-toxic environment that is conducive to innovation and the development of sustainable substitutes including non-chemical solutions."

Box 4.1 Chemical innovation for sustainability

Sweden has recently established a Chemical Substitution Centre at the state-owned RISE Research, to help smaller companies replace hazardous chemicals. The Centre aims both to stimulate the development of sustainable chemical products, production processes, articles and non-chemical methods, and to build capacity in the public and private sector. This will contribute to developing greener products and a circular economy.

One example is to find and implement better alternatives for the problematic, highly fluorinated compounds such as PFAS in consumer goods such as textiles, cosmetics and food-packaging.

Alongside this, the EU action plan for a circular economy contains measures covering the whole product cycle: from production and consumption to waste management and the market for secondary raw materials (COM, 2015). Seen in this light, harmful chemicals used in products can present a barrier for materials to be recycled. Finding new ways to deliver the desired benefit represents opportunity for innovation (box 4.1).

Radically rethinking our existing approach to chemicals has followed. From an environmental perspective, given the thousands of chemicals in daily use, it is not sustainable to regulate a chemical, then measure it in

the environment and assess whether it is causing harm. However, managing the current situation into the next few decades requires dealing with chemicals already in use (Box 4.2). The following sections describe some EU and national approaches to limiting the harm presented by chemical pollution.

Box 4.2 – Chemicals for a sustainable future

 $\frac{https://www.eea.europa.eu/about-us/governance/scientific-committee/reports/chemicals-for-a-sustainable-future$

Regulation of chemicals is entering a new phase as we better understand the diversity and persistence of substances in the environment. Key issues are :

Chemical production is increasing and poses risks to ecosystems and human health.

European legislation has reduced acute pollution, but chronic, less apparent effects persist.

Environmental and societal megatrends are changing exposure patterns.

Chemical risks are traditionally underestimated by science.

A focus on critical parameters is more important than gathering more general data.

Monitoring for a wider variety of chemicals can provide earlier warnings.

Policy approaches need to be further integrated in support of sustainability objectives.

Avoiding upstream use of persistent and hazardous chemicals is key.

A less toxic environment requires visionary and inclusive stakeholder approaches.

4.2. EU strategic approach to pharmaceuticals in the environment

The 2013 Priority Substances Directive required the European Commission to develop a strategic approach to pollution of water by pharmaceutical substances, with expectation that the strategy would be developed by 2015. (The strategic approach was scheduled for adoption by the Commission in 2018, but at the time of writing no date for adoption has been set.) Cutting across health and environment legislative policies, pharmaceuticals in the environment is a "headline grabbing" topic where balancing the needs of different stakeholders is challenging and essential. Building understanding and developing effective, proportionate actions across different areas requires resources and high level commitment. While the EU level approach is being developed, Member States continue to develop actions relevant to their competence.

4.2.1. The issue

Pharmaceuticals are used to improve the health of both humans and animals. Once taken, the medicine and its breakdown products ("metabolites") are excreted in urine and fæces. Where there is urban waste water treatment, sewage is treated and the medicine and its breakdown products may be broken down further. Substances remaining may then be discharged into the environment, in effluent or as sewage sludge applied to land.

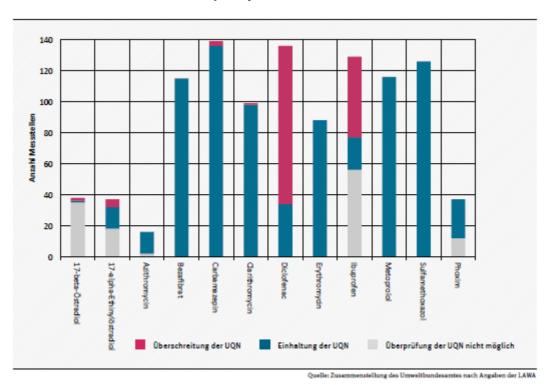
EU medical products regulation (EC, 2004) requires environmental risk assessment for veterinary medicines, but that is not currently required for human medicines. This in part reflects the tensions in priorities between the benefits of health care and risks to drinking water resources and ecosystems. As understanding of the potential effects of very low levels of pollutants has increased, so has concern about release of biologically active molecules into the environment.

4.2.2. Member State responses

There was collaboration between Member States and the Commission well in advance of the Priority Substances Directive (EU, 2013b). Two-way communication – advising of concerns and learning about them – is part of a well-functioning, high level process. Possible EQS values were prepared, and although these did not become legally binding, they are used to indicate whether there may be concentrations of concern.

To differing extents, Member States were investigating concentrations of medicines in their surface waters. For example, further to investigations into effects of a contraceptive pill ingredient, EE2, on fish, work in the UK considered waste water treatment and socioeconomic impacts of pharmaceuticals in the environment (Environment Agency, 2008; Gardner et al, 2013; Defra, 2015). In Germany, between 2013–2015, concentrations of several pharmaceuticals were compared with possible EQS, revealing isolated cases where EQS were exceeded for carbamazepine (an anti-epileptic), clarithromycin, the contraceptives E2 and EE2, and more frequently in the cases of diclofenac and ibuprofen (Figure 3.2).

Figure 4.2 Pharmaceuticals in German Surface Waters: Comparison of annual concentration means at surveillance monitoring sites with possible environmental quality standards



Source: Waters in Germany – Status and Assessment. Federal Environment Agency, 2017. https://www.umweltbundesamt.de/sites/default/files/medien/377/publikationen/171018_uba_gewasser dtl_engl_bf.pdf

4.3. National Action Plans to reduce risks from pesticides 13

EU legislation can require Member States to derive national approaches where that is appropriate. For example, the "Sustainable Pesticide Use Directive" (EC, 2009b) required that

 $^{{}^{13}\}underline{https://www.nap-pflanzenschutz.de/en/about-the-national-action-plan/regulations/european-regulations/directive-2009128ec/\ accessed\ 25/03/2018)}$

Member States introduce National Action Plans, setting objectives, measures and timelines to reduce risks for human health and the environment by the end of 2012.

- training of users, advisors and distributors
- inspection of pesticide application equipment
- the prohibition of aerial spraying
- the protection of the aquatic environment and drinking water
- limitation of pesticide use in sensitive areas
- information and awareness raising about pesticide risks
- systems for gathering information on pesticide acute poisoning incidents, as well as chronic poisoning developments, where available.

4.4. National action programs for combating risks from micropollutants

To protect their citizens and the environment, some Member States have initiated national programmes and strategies to reduce the risks posed by substances harmful at low concentrations ("micropollutants"). Examples of such programmes are:

- The Swedish MistraPharma Project 2008-15 worked to identify human pharmaceuticals that are likely to be of concern to aquatic ecosystems, and addressed the risk for antibiotic resistance promotion in the environment¹⁴. It also proposed risk management strategies, in particular improved regulatory test requirements and waste water treatment technologies.
- In France, a comprehensive monitoring program was established on micropollutants, the "*National plan against micro-pollutants 2016- 2021*" It aims to reduce micropollutant emissions in order to protect water quality and biodiversity to preserve water quality and biodiversity.
- In Britain, United Kingdom Water Industry Research (UKWIR) collaborate upon the "Chemicals Investigation Programme" (CIP), as a response to current and emerging legislation on trace substances in the water environment, bringing together water and waste water companies in England and Wales with regulators (Gardner et al, 2012, 2014). CIP phase 1, 2010-14, obtained a comprehensive view of concentrations in effluents for over 70 contaminants, finding that the principal source of many trace contaminants is domestic. The second phase, comprises sampling of 74 substances at over 600 sewage treatment plants. Substances of interest include metals, industrial chemicals such as fire retardants and biocides, hydrocarbons, pharmaceuticals, hormones and personal care products. The research program has examined several

¹⁴ http://www.mistrapharma.se/ (accessed 26/03/2018)

¹⁵https://www.ecologique-

solidaire.gouv.fr/sites/default/files/National%20plan%20against%20micropollutants%202016-2021%20to%20preserve%20water%20quality%20and%20biodiversity.pdf accessed 29/08/2018

- novel waste water treatment techniques that can be used to supplement existing processes.
- The *Pharmaceutical Chain Approach* is a Dutch strategy, which considered the life cycle of pharmaceuticals from development, authorisation, prescription, use and wastewater treatment. End of pipe measures, e.g. wastewater treatment are seen as complementary to measures in the health sector. With a focus on pharmaceuticals a set of programs was started in the Netherlands. These are inter alia the programs: medicines out of water's, public communication strategies on the reduction of antibiotic use and substitution of certain drugs by others that are less harmful to the environment (Grinten, et al., 2016)¹⁶.

4.5. Summary

Regulation to protect water quality is core to protecting public health and the environment. Many approaches are possible: the challenge now is perhaps to ensure that there is coherence between different activities. While the WFD greatly facilitates coherence in water management, activities around chemicals may not be so well aligned. For instance, efforts to reduce air pollution may lead to discharges to water when pollutants are filtered out of gaseous emissions.

It should be understood that the cycling of chemicals "from cradle to grave" can lead to water pollution if not adequately managed. Long term strategies towards a circular economy and a non-toxic environment hold the promise of ceasing chemical pollution in future. However, for the medium term, practical approaches to preventing pollution by existing products and substances continue to be required.

64 Chemicals in Europe's surface waters

https://www.daarwordtiedereenbetervan.nl/ (26th March 2018)
https://jamdots.nl/view/239/Medicijnresten-uit-water (26th March 2018)

5. Improving protection against chemical risks in water

5.1. Introduction

Earlier chapters discussed approaches to tackle the significant concern that we are failing to adequately protect aquatic ecosystems from mixtures of low concentrations of chemicals, and reviewed information available for established water pollutants. Once released into the aquatic environment, persistent, harmful chemicals are very difficult to control and may have long-lasting effects. We need effective ways to protect our water resources, so as to ensure their long term sustainability.

Two major challenges confront our understanding of chemicals in surface waters across Europe. The first is that, despite significant effort, we struggle to show that at the European level there have been improvements in the environment resulting from increased controls of the most well-known pollutants. The second is that chemical status under the WFD reflects scientific understanding that is at least 20 years old.

Headline chemical status is driven by the "one out all out" approach of the WFD, where the status reflects that of the worst component. For chemicals, the pass/fail nature of the EQS means that the failure of one priority substance or one RBSP will lead to the water body failing to achieve good status. Although it is possible to see improvements in individual priority substances (EEA, 2018a), the revision of EQS and addition of new priority substances to reflect better understanding of chemical risks represents recurrent new challenges to achieving good chemical status. This difficulty is more than a "communications issue". Maintaining political support and resources towards improved environmental protection is difficult at every level when little, no, or even negative progress is made.

There is a need to be able to communicate about improvements made according to the standards when they were set. Equally, the WFD needs to reflect robust, new scientific understanding which identifies new risks. This chapter reflects on the findings of earlier chapters and proposes some possible ways forward.

5.2. Data collection on chemicals in water at EU level

Significant effort goes into reporting into the European system and then in making that information available. In the light of Peter Drucker's observation, "if you can't measure it, you can't change it", we reviewed what was available for key chemical pollutants.

5.2.1. Data on chemical status and priority substances

Monitoring obligations need to balance costs of resources to undertake them, with the value of the knowledge gained and application of that knowledge. Collecting data which have no application is not only wasted effort, it may mean that an opportunity is missed to gather information which would be used to inform measures.

What should be a priority substance? A working basis for a "European level pollutant" is provided by the prioritisation process, which considers a substance to be of European concern if it exceeds proposed EQS in 4 or more Member States (JRC, 2016). Following reporting of the second River Basin Management Plans, the continuing relevance of a priority substance can be considered. (table 5.1).

Table 5.1: Priority substances which exceed EQS in less than 15 (out of 111 105) surface water bodies and 4 or fewer Member States

Priority Substance	Type / use of chemical		No. of Member States reporting that good chemical status not achieved
Atrazine	Herbicide	9	4
Dichloromethane	Industrial	6	4
Chloroalkanes C10-13	Industrial	5	4
Tetrachloroethylene	De-greaser, dry cleaning	6	3
Chlorfenvinphos	Pesticide	5	3
Alachlor	Herbicide	5	3
Pentachlorophenol	Pesticide, disinfectant	3	3
Pentachlorobenzene	Industrial	7	2
Trichloroethylene	Industrial	4	2
Trichlorobenzenes	Industrial	3	2
Simazine	Herbicide	4	1
1,2-dichloroethane	Industrial	1	1
Carbon tetrachloride	Refrigerant, fire-fighting	1	1

Source:

Preliminary results based on WISE-SoW database) including data from 25 Member States (EU28 except Greece, Ireland and Lithuania).

The very low numbers of water bodies failing for these substances suggest that, assuming monitoring and reporting are accurate, measures have been effective in preventing the entry of these chemicals into surface waters. This is a success for European water and chemicals policies.

With such low numbers of water bodies failing to achieve good status for these substances, they may be candidates for delisting as priority substances, freeing up resources for monitoring of substances now presenting more of a risk to the quality of European waters.

It is also possible to review River Basin Specific Pollutants to identify those which might have European wide relevance (table 5.2). RBSPs most often exceeding their EQSs are shown, with the range in EQS values used (derived from Member States RBMP reporting).

Table 5.2 Selected River Basin Specific Pollutants with largest numbers of countries reporting failures; Comparison of minimum and maximum national standards for annual average EQS.

Name of Substance	No. Member States with EQS exceedance	waterbodies exceeding	Min (ug/l)	Max (ug/l)	Median (ug/l)
Zinc	18	1 454	0	1000	18
Copper	16	808	0	120	9
Arsenic	14	385	0	50	10
Chromium	10	110	0	50	5.5
Total cyanide Free cyanide	4 5 ⁽¹⁾	47 25	0.3 1	50 50	5 5
MCPA	6	159	0.1	1.6	0.6
Terbuthylazine	6	51	0.2	1	0.35
Metolachlor	5	115	0.1	1	0.1
2-4D	4	18	0.1	20	0.3
Malathion	4	13	0.0008	0.2	0.01
Parathion	4	7	0.0002	0.01	0.005

Note: Data from RBMP reporting differ from those reported by Irmer et.al. (2014) which were derived from voluntary reporting.

https://tableau.discomap.eea.europa.eu/t/Wateronline/views/WISE_SOW_FailingRBSP/SWB_FailingRBSP_Europe?:embed=y&:display_count=no&:showVizHome=no_(30 Aug 2018)

Decisions on what substances are proposed as priority substances are made through the collaborative process under the WFD, prior to a Commission proposal subject to the codecision process. It is currently unclear when the next revision to the list of priority substances may be made.

Guidelines for EQS derivation are set in the technical guidance document for environmental quality standards (EC, 2011b). Although such documents should promote coherence and harmonisation, EQS values can differ by up to 10 000 times for the same substance (e.g. phenol, glyphosate) (Irmer, et al, 2014).

As well as variation in values of EQS, there can be significant differences in numbers of RBSPs between Member States – between 1-136 RBSPs were reported as causing failure in the 2nd

⁽¹⁾ -1 country had standards for both free and total cyanide, hence 8 countries reported in table 2.1. Source

RBMPs¹⁷. This has an influence on the likelihood of an RBSP failing to meet an EQS, and so the likelihood of a water body being able to achieve good ecological status. More RBSPs make it more likely that a water body may not meet the EQS.

Looking forward, it would seem that improving consistency (or harmonising) RBSP EQS values would improve comparability between river basin districts. It would not address differing numbers of substances for which standards are set, and, given the variation across Europe of substances meeting the RBSP definition, it seems difficult to overcome that issue. Consideration should be given to including all chemicals information in one place, e.g. chemical status, reflecting actual water management, if other ways are found to better integrate chemical and ecological status.

5.2.2. Emissions to water

Reporting known or estimated chemical emissions is a way to gather information on trends over time, without knowing what impact those might have. Unfortunately, emissions data on priority substances as reported for the WFD, E-PRTR and WISE-SoE are only partially informative. The WFD dataset is difficult to interpret, with apparent errors, inconsistencies and missing river basin districts.

Lack of comparable information at EU level on diffuse sources of pollution to water represents a potentially significant gap (Roovaart et al, 2013a and b).

Given these significant concerns, what can we see in the data?

Table 3.2 provided an overview of the number of Member States reporting of emissions in 2010 for the different source groups: industry, UWWTPs and diffuse sources.

The metals cadmium, lead, mercury and nickel were widely reported, but even for these long-regulated substances are there difficulties with the data reporting. While a range of diffuse sources were reported for metals, different approaches in calculation between the countries render those data incomparable.

For another set of pollutants, about half of the countries reported on a regular basis (some PAHs, 4-Nonylphenol, DEHP). Although this allows for some overview at European level, there were difficulties with the data from different reporting streams (E-PRTR, WFD, WISE-SoE), making interpretation of trend difficult.

For a number of pollutants, only a few Member States report loads (TBT, Brominated diphenylethers, Isoproturon, hexachlorocyclohexane). Therefore, no useful overview exists for these pollutants at EU level.

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Diffuse sources of pollution have been reported by only a few countries, even though – where they are reported – they seem to constitute a large proportion of diffuse sources for almost all priority substances (Roovaart et al, 2017). This represents a significant data gap.

Ways forward:

- Currently, data on emissions are required under EU legislation for both EPRTR and WFD, and are voluntarily reported under WISE SoE. Improving emissions data so that they are collected under consistent and comparable approaches would provide clear information on the direction of travel for chemical pressures. This could be especially helpful for substances where the surface water chemical status assessed under WFD is driven by historic rather than current emissions. Streamlining reporting, so that robust data collected for one obligation would satisfy the European emissions reporting requirement, could offer a way to address this issue.
- As point sources of pollution are better controlled, so the relative significance of diffuse sources increases. Our lack of knowledge about diffuse emissions represents an important information gap. Improvement in the monitoring and reporting of diffuse sources is needed, to ensure that pressures are correctly understood and measures can be appropriately targeted.

5.3. Conclusions on assessing ecological impacts from chemical pollution

The chemical status of surface waters, reported under the WFD, provides an assessment of a very limited number of harmful chemicals in water bodies comparable across Europe. Much more detailed information on chemical contamination can be available at a more local scale. Through scientific efforts like the application of novel methods of sampling and chemical enrichment (Schulze et al. 2017), the detection of several hundred organic chemicals in a single freshwater sample is becoming more common.

Currently, there is no established link between the assessment of chemical status and ecological status of surface water bodies. This is in contrast to the real situation where organisms may be living in polluted water, possibly impacted by multiple pressures. Improvements in our understanding as to how chemical mixtures can adversely impact organisms may be used to improve our understanding of the interlinkage between ecological status and chemical status. Application of the precautionary principle means this should include consideration of chemical mixtures, which can act along similar pathways in the organism. However, potential consequences of the presence of multiple chemicals is not reflected in current lists of priority substances and RBSPs.

More generic solutions are needed to protect water from contamination by chemicals. Approaches which regulate concentrations in water on a substance-by-substance approach will not cope with large numbers of substances present at apparently low concentrations but which might, in combination, have ecological effects. Effects-based approaches offer a way to combine existing information on the presence and abundance of species in ecological monitoring, while improving our understanding of the links between chemical and ecological information. The flexible approach of the WFD would allow Member States to use effects-based methods in a complementary way, alongside routine monitoring in water management. The major obstacles to the use of such tools seem to be the mis-alignment with chemicals source control approach, aimed at single substances, and the lack of legal obligation. In the

absence of legal requirement, one way to demonstrate the value would be to collect case studies where effect-based information has been used in a regulatory context for surface waters. One option could be for effects-based methods to be used as part of ecological status assessment.

5.4. Conclusions on the effectiveness of source control legislation

Reported emission data do not allow quantitative conclusions about the effectiveness of source control measures taken in the past. The data are not sufficiently reliable and the time series are not long enough for analysis. However, emission loads should have decreased, driven by the implementation of the directives on Dangerous Substances (1976), Urban Waste Water (1991) and Industrial Emissions (2010). Additionally, chemicals are now widely regulated and environmental concerns reflected in risk and hazard assessments (chapter 1.3).

Over recent decades, reductions in emissions from industry have led to significant sources now being from domestic use (Gardner et al, 2014). Despite much tighter regulation, pesticide use in agriculture can still cause contamination. Events such as heavy rainfall can overload drainage systems and cause surges in the pollutant load into surface waters.

We rely on urban waste water treatment to reduce concentrations of many pollutants in water, but they may not meet sufficiently low concentration of micro-pollutants such as pharmaceuticals, ingredients of household chemicals, chemicals used in small businesses or industries, or pesticides. Investigations into more advanced waste water treatment techniques, for the elimination of micro-pollutants via a fourth treatment stage, are being tested in several countries. Such techniques cost about 10 to 15 EURO cents per m³ in big treatment plants, but they are not yet applied on a regular basis (UBA, 2018).

Table 5.1 showed examples of substances for which measures to prevent water pollution seem to have been effective. Sometimes this involved totally banning the use of a substance; less drastic measures may be to restrict uses where losses to water might occur, either through more careful use of the substance (such as in good practice for pesticide application) or banning its use in certain applications because such measures are not possible.

In this report, the focus has been on priority substances continuing to present a risk to Europe's surface waters. Table 5.3 summarises the current situation and considers what more could be done to improve environmental protection.

Table 5.3 – Effectiveness of controls to prevent chemicals reaching aquatic environment from point sources

Priority Substance	Emissions data – point sources¹ (data on all diffuse are weak)	Historic contaminant ³ / natural sources	No. waterbodies failing to achieve good chemical status ²	Chemical status reflects emissions which are	What more needs to be done to protect the environment
Contamination ma	ainly through	atmospheric c	leposition (sect	ion 2.4)	
Mercury ⁴	Strong	Yes	Many	Mainly earlier	Maintain efforts to cease emissions

					from human activities	
Benzo(g,h,i)perylene + Indeno(1,2,3-cd)-pyrene	Weak	Yes	Medium		Improve understanding of	
Fluoranthene	Moderate	Yes	Medium		significant sources to water. Improve efforts to reduce atmospheric emissions from burning of organic matter; Reduce road run-off	
Benzo(a)pyrene	Weak	Yes	Medium	Current and		
Benzo(b)fluoranthene + Benzo(k)fluoranthene	Weak	Yes	Low	earlier		
Anthracene	Moderate	Yes	Low			
Contaminatio	n mainly fron	n urban settler	nents (section	2.5)		
DEHP	Moderate - Strong	No	Low	Current	Prevent new uses and improve urban	
4-Nonylphenol	Moderate - Strong	No	Low		waste water treatment.	
Brominated diphenylethers ⁴	Weak	No	Many	Current and earlier	Improve understanding of pathways to water. Waste management of furniture etc containing PBDEs to prevent releases	
Contamination	mainly from	industry and i	mining (section	า 2.6)		
Cadmium	Strong	Yes	Low		Maintain efforts to	
Nickel	Strong	Yes	Low		minimise losses from industry and	
Lead	Strong	Yes	Low	Current and earlier	urban waste water treatment. Provide treatment facilities and remediation at (old) mining areas.	
Contamin	ation mainly	from agricultu	re (section 2.7))		
Hexachlorocyclohexane ⁴	Weak	No	Low	Mainly earlier		
Isoproturon	Weak	No	Low	Current and earlier ⁵	Enforce new restriction	
Contamin	ation mainly	from navigation	on (section 2.8)			
Tributyltin-cation ⁴	Weak	No	Low	Mainly earlier	Ensure non- restricted uses do not cause releases	

Note – Information on diffuse sources is mostly poor, so excluded from this table.

Moving beyond the well-established pollutants represented by priority substances, we need to implement methods which effectively assess the risk presented by mixtures in the aquatic environment. Longer term sustainability can be provided by the development of alternative

^{1 -} see Table 3.2

^{2 –} table 3.1 based on 111 105 water bodies and number of water bodies failing for substance (Many = over 10 000; Medium = over 1 000; Low = over 100)

 $^{3 - \}text{Historic} = \text{use before } 1940$

^{4 –} International restrictions as POPS

⁵ – regulatory approval for isoproturon expired in 2017, so data reflect the period where its use was still permitted

approaches which deliver the desired function currently provided by harmful chemicals. Developing a circular economy is part of this process.

6. References

Abdel-Shafy, H. and Mansour, M, 2016 A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. Egyptian Journal of Petroleum Volume 25, Issue 1, March 2016, Pages 107-123.

AbwV, 1997. Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer (Abwasserverordnung - AbwV). (https://www.gesetze-im-internet.de/abwv/AbwV.pdf) accessed 3 September 2018

AMAP/UNEP, 2015. Global Mercury Modelling: Update of Modelling Results in the Global Mercury Assessment 2013. Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland.

Altenburger, R., S. Ait-Aissa, P. Antczak, T. Backhaus, D. Barceló, T.-B. Seiler, F. Brion, W. Busch, K. Chipman, M. L. de Alda, G. de Aragão Umbuzeiro, B. I. Escher, F. Falciani, M. Faust, A. Focks, K. Hilscherova, J. Hollender, H. Hollert, F. Jäger, A. Jahnke, A. Kortenkamp, M. Krauss, G. F. Lemkine, J. Munthe, S. Neumann, E. L. Schymanski, M. Scrimshaw, H. Segner, J. Slobodnik, F. Smedes, S. Kughathas, I. Teodorovic, A. J. Tindall, K. E. Tollefsen, K.-H. Walz, T. D. Williams, P. J. Van den Brink, J. van Gils, B. Vrana, X. Zhang and W. Brack (2015). Future water quality monitoring—Adapting tools to deal with mixtures of pollutants in water resource management. Sci Total Environ 512–513:540–551.

Altenburger, R., Scholze, M., Busch, W, Escher, B., Jakobs, G., Krauss, M., Krüger, J., Neale, P.A., Ait-Aissa, S., Almeida, A.C., Seiler, T.B., Brion, F., Hilscherová, K., Hollert, H., Novák, J., Schlichting, R., Serra, H., Shao, Y., Tindall, A., Tolefsen, K.E., Umbuzeiro, G., Williams, T.D., Kortenkamp, A., 2018. Mixture effects in samples of multiple contaminants - An interlaboratory study with manifold bioassays. Environ Int., 114: 95-106

Anderson J.D., MacRae (2006). Polybrominated diphenyl ethers in fish and wastewater samples from an area of the Penobscot River in Central Maine. Chemosphere 62, 7, p. 1153-1160. https://doi.org/10.1016/j.chemosphere.2005.06.034

Ankley et al. 2010. Adverse outcome pathways: a conceptual framework to support ecotoxicology research and risk assessment. Environ Toxicol Chem. 29(3):730-41.

Arle, J., Mohaupt, V., Kirst, 2016. Monitoring of Surface Waters in Germany under the Water Framework Directive—a Review of Approaches, Methods and Results. Water 8, no. 6 (2016): 217.

Baker, D.R., Kasprzyk-Hordern, B., 2013. Spatial and temporal occurrence of pharmaceuticals and illicit drugs in the aqueous environment and during wastewater treatment: new developments. Sci. Total Environ. 454-455, 442-456.

Beckers, L-M., Busch, W., Krauss, M., Schulze, T., Brack, W., 2018. Characterization and risk assessment of seasonal and weather dynamics in organic pollutant mixtures from discharge of a separate sewer system. Water Research 135, 122-133 https://doi.org/10.1016/j.watres.2018.02.002

Birk, S., Bonne, W., Borja, A., Brucet, S., Courrat, A., Poikane, S., Solimini, A.G., Bund, W. van de, Zampoukas, N. & Hering, D. (2012) Three hundred ways to assess Europe's surface waters: an almost complete overview of biological methods to implement the Water Framework Directive. Ecological Indicators, 18, 31-41.

Brack, W., Dulio, V., Ågerstrand, M., Allan, I., Altenburger, R., Brinkmann, M., Bunke, D., Burgess, R.M., Cousins, I., Escher, B.I., Hernández, F.J., Hewitt, L.M., Hilscherová, K., Hollender, J., Hollert, H., Kase, R., Klauer, B., Lindim, C., López Herráez, D., Miège, C., Munthe, J., O'Toole, S., Posthuma, L., Rüdel, H., Schäfer, R.B., Sengl, M., Smedes, F., van de Meent, D., van den Brink, P., van Gils, J., van Wezel, A.P., Dick Vethaak, A., Vermeirssen, E., von der Ohe, P.C., Vrana, B., (2017): Towards the review of the European Union Water Framework Directive: Recommendations for more efficient assessment and management of chemical contamination in European surface water resources. *Sci. Total Environ.* **576:**720-737

Brack et al. 2016. Effect-directed analysis supporting monitoring of aquatic environments — An in-depth overview. Sci. Total Environ. 544:1073 - 1118

Brack, W., Altenburger, R., Schüürmann, G., Krauss, M., López Herráez, D., van Gils, J., Slobodnik, J., Munthe, J., Gawlik, B.M., van Wezel, A., Schriks, M., Hollender, J., Tollefsen, K.E., Mekenyan, O., Dimitrov, S., Bunke, D., Cousins, I., Posthuma, L., van den Brink, P.J., López de Alda, M., Barceló, D., Faust, M., Kortenkamp, A., Scrimshaw, M., Ignatova, S.N., Engelen, G., Massmann, G., Lemkine, G., Teodorovic, I., Walz, K.-H., Dulio, V., Jonker, M.T.O., Jäger, F., Chipman, K., Falciani, F., Liska, I., Rooke, D., Zhang, X., Hollert, H., Vrana, B., Hilscherova, K., Kramer, K., Neumann, S., Hammerbacher, R., Backhaus, T., Mack, J., Segner, H., Escher, B., Umbuzeiro, G.A., (2015): The SOLUTIONS project: Challenges and responses for present and future emerging pollutants in land and water resources management. Sci. Total Environ. 503-504:22 – 31

Busch et al. 2016. Micropollutants in European Rivers: A Mode of Action Survey to Support the Development of Effect-Based Tools for Water Monitoring. Environ Toxicol Chem 35:1887–1899.

CIRCABC, 2005. Substance EQS Data Sheets.

(https://circabc.europa.eu/faces/jsp/extension/wai/navigation/container.jsp?FormPrincipal: idcl=FormPrincipal: id1&FormPrincipal: idcl=FormPrincipal: id1&FormPrincipal: idcl=FormPrincipal: idcl=FormPrincipal: id1&FormPrincipal: idcl=FormPrincipal: idcl=FormPrincipal

149f6667c19f&javax.faces.ViewState=q%2B6kZwzCgKS05wJnTnGv5khT%2B1kOkbmUu56XntrwXciTUJMqcUOtEa77fJeWao9SVquqWHcS192t9O156lqxxPweccHhzRsWhamob4008d9k4ApyG0%2BbxmB81jZRYqnUkhUy9qmojmZ39EBSmGDeVXJJCTc%3D) accessed 3 September 2018.

COM, 2015. Closing the loop - An EU action plan for the Circular Economy. COM(2015) 614 final (https://eur-lex.europa.eu/resource.html?uri=cellar:8a8ef5e8-99a0-11e5-b3b7-01aa75ed71a1.0012.02/DOC_1&format=PDF) accessed 3 September 2018.

COM – DG ENV, 2017. Background document for public consultation on pharmaceuticals in the environment

Defra (2015) Review of socioeconomic impacts of pharmaceuticals in the water environment. Technical report WT1544.

Doppler, T., Mangold, S., et al. 2017. Hohe PSM-Belastung in Schweizer Bächen. Aqua & Gas, No. 4, 46-56.

74 Chemicals in Europe's surface waters

Earnshaw. M., Jones, K., Sweetman, A. (2013). Estimating European historical production, consumption and atmospheric emissions of decabromodiphenyl ether. Sc. Tot. Env. 447, p. 133-142. https://www.sciencedirect.com/science/article/pii/S0048969712016063

EC, 1973. Programme of Action of the European Communities on the Environment. OJ C 112/1. 20.12.1973. (https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=OJ:C:1973:112:FULL&from=EN) accessed 3 September 2018

EC, 1989. Directive (89/106/EC) of the Council of 22 December 1988 on the approximation of laws, regulations¬ and administrative provisions of the Member States relating to construction products, OJ L 40, p. 12, most recently amended by Article 65 of the Adaptation Directive (EU) 305/2011 of 9 March 2011, OJ L 88, p. 5.

EC, 2001. Directive 2001/42/EC of the European Parliament and of the Council of 27 June 2001 on the assessment of the effects of certain plans and programmes on the environment, OJ L 197, p. 30 ff.

EC, 2003. Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether).

EC, 2004. Regulation (EC) No 726/2004 of the European Parliament and of the Council of 31 March 2004 laying down Community procedures for the authorisation and supervision of medicinal products for human and veterinary use and establishing a European Medicines Agency, OJ L 136, p. 1–33

EC, 2006a. Directive 2006/11/EC of the European Parliament and of the Council of 4 March 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, OJ, L 64, p. 52 ff (formerly Directive 76/464/EEC).

EC, 2006b. Regulation (EC) No. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EEC (Reg. (EC) No. 166/2006), OJ L 33, p. 1.

EC, 2007. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, OJ L 396, p. 1.

EC, 2008a. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC and 86/280/EEC and amending Directive 2000/60/EC, OJ L 348, p. 84 ff., amended with 2013/39/EU on 12 August 2013, OJ L 226, p. 1, 6.

EC, 2008b. Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a framework for Community action in the field of marine environmental policy, OJ L 164, p. 19 ff.

EC, 2008c. Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006, OJ L 353, p. 1.

EC, 2009a. Regulation (EC) No. 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC, OJ L 309, p. 1 ff.

EC, 2009b. Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides, OJ L 309, p. 71 ff.

EC, 2010. Directive (2010/75/EU) of the EP and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control), OJ L 334, p. 17, recast OJ 2012 L 159, p. 25.

EC, 2011a. Polycyclic aromatic hydrocarbons factsheet. JRC technical notes JRC 66955-2011.

EC, 2011b. CIS Guidance No. 27 Deriving Environmental Quality Standards. (http://ec.europa.eu/environment/water/water-framework/facts-figures/guidance-docs-en.htm) accessed 3 September 2018.

EEA, 2001. Late lessons from early warnings. EEA report 22/2001.

EEA, 2011. Hazardous substances in Europe's fresh and marine waters, https://www.eea.europa.eu/publications/hazardous-substances-in-europes-fresh

EEA, 2012. European Waters – Assessment of Status and Pressures. https://www.eea.europa.eu/publications/european-waters-assessment-2012/at_download/file

EEA, 2013. Late lessons from early warnings II. EEA Report 1/2013.

EEA, 2015a. ETC-ICM technical reports 3/2015 on hazardous substances. (http://icm.eionet.europa.eu/ETC_Reports/HazardousSubstancesInWater_2015) accessed 3
September 2018

EEA, 2015b. Waterbase_2015_v1_WISE1: https://www.eea.europa.eu/data-and-maps/data/waterbase-emissions-5, last modified 11 Oct 2016.

EEA, 2017a. E-PRTR database version 11: https://www.eea.europa.eu/data-and-maps/data/member-states-reporting-art-7-under-the-european-pollutant-release-and-transfer-register-e-prtr-regulation-14, last modified 18 aug 2017.

EEA, 2017b. WFD-dataset: data_WFD2016_V_2_14, 17/08/2017.

EEA, 2017c. Emissions of pollutants to Europe's waters - sources, pathways and trends. ETC-ICM technical report 3/2017.

(http://icm.eionet.europa.eu/ETC_Reports/EmissionsOfPollutantsToEuropeanWaters_SourcesPathwaysAndTrends) accessed 3 September 2018

EEA, 2018a: European Waters – Assessment of Status and Pressures 2018. Copenhagen.

EEA, 2018b. European Pollutant Release and Transfer Register http://prtr.eea.europa.eu/#/pollutantreleases Accessed 4th September 2018

EEA, 2018c. Air pollutant emissions dataviewer (LRTAP Convention) https://www.eea.europa.eu/data-and-maps/dashboards/air-pollutant-emissions-data-viewer-1 accessed 05/09/2018.

EEC, 1982. Council Directive 96/82/EEC of 9 December 1996 on the control of major-accident hazards involving dangerous substances, OJ L 10, p. 13 ff., most recently amended by Regulation (EC) No. 1137/2008 of the European Parliament and of the Council of 22 October 2008, OJ L 311, p. 1, 17. The Directive was repealed on 1 July 2015 and replaced by Directive 2012/18/EU, OJ L 197, p. 1.

EEC, 1986. 86/278/EEC Council Directive on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture.

EEC, 1991a. Council Directive 91/271/EEC of 21 May 1991concerning urban waste-water treatment. OJ L 135, p. 40 ff., most recently amended by Regulation (EC) No. 1137/2008 of the European Parliament and of the Council of 22 October 2008, OJ L 311, p. 1, 14.

EEC, 1991b. Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources, OJ L 375, p. 1 ff., most recently amended by Regulation (EC) No. 1137/2008 of the European Parliament and of the Council of 22 October 2008, OJ L 311, p. 1, 15.

EEC, 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, OJ L 330, p. 32 ff, most recently amended by Annex 2.2 to the Adaptation Regulation (EC) 596/2009 of 18 June 2009, OJ L 188, p. 14 (formerly Directive 76/160/EEC).

Egebäck, A.-L., Sellström, U., McLachlan, M.S. (2012). Decabromodiphenyl ethane and decabromodiphenyl ether in Swedish background air. Chemosphere, 86, 3, p 264-269. https://doi.org/10.1016/j.chemosphere.2011.09.041

EMEP, 2017.

http://webdab1.umweltbundesamt.at/scaled_country_year.html?cgiproxy_skip=1

Environment Agency 2008. Long-term exposure to environmentally relevant concentrations of ethinyloestradiol affects sexual differentiation and development in roach, Rutilus rutilus. Science Report – SC030299/SR2

Environment Agency, 2013. Nonylphenol ethoxylates in imported textiles. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/296853/13_04_29_Rpt_NPE_textiles_summary_report_LIT_7721_5b9cd4.pdf accessed 20 August 2018.

EPA, 2017. Technical Fact Sheet – Polybrominated Diphenyl Ethers (PBDEs). EPA 505-F-17-015

EPRS 2015. The Precautionary Principle. PE 573.876 http://www.europarl.europa.eu/RegData/etudes/IDAN/2015/573876/EPRS_IDA(2015)573876_EN.pdf

Escher at al. 2014. Benchmarking Organic Micropollutants in Wastewater, Recycled Water and Drinking Water with In Vitro Bioassays. Environ. Sci. Technol., 2014, 48 (3), pp 1940–1956

EU, 2011. Directive 2011/92/EU of the European Parliament and of the Council of 13 December 2011 on the assessment of the effects of certain public and private projects on the environment, OJ 2012 L 26, p. 1.

EU, 2012. Regulation (EU) No. 528/2012 of 22 May 2012 concerning the making available on the market and use of biocidal products, OJ L 167, p. 1.

EU 2012. Commission Regulation (EU) No 252/2012 of 21 March 2012 laying down methods of sampling and analysis for the official control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EC) 1883/2006, OJ L 84, 23.03.2012, p. 1

EU, 2013a. Decision No 1386/2013/EU of the European Parliament and of the Council of 20 November 2013 on a General Union Environment Action Programme to 2020 'Living well, within the limits of our planet', Annex A, paragraph 54e (OJ L 354, 28.12.2013, p. 171–200).

EU, 2013b. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. OJ L 226, 24.8.2013, p. 1–17.

EU, 2016. Commission Implementing Regulation (EU) 2016/872 of 1 June 2016 concerning the non-renewal of approval of the active substance isoproturon, in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market, and amending Commission Implementing Regulation (EU) No 540/2011; OJ L 145, p. 7, 9

Eurostat, 2018. Agri-environmental indicator — consumption of pesticides https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-consumption_of_pesticides (accessed 05/09/2018)

FGG Weser, 2016. Flussgebietsgemeinschaft Weser (2016). Bewirtschaftungsplan 2015 bis 2021 für die Flussgebietseinheit Weser gemäß §83 WHG (https://www.fgg-weser.de/component/jdownloads/send/8-eg-wrrl/331-bwp2015-weser-final-textteil-160318) accessed 3 September 2018.

Fliedner, A., N. Lohmann, H. Rüdel, D. Teubner, J. Wellmitz and J. Koschorreck (2016). Current levels and trends of selected EU Water Framework Directive priority substances in freshwater fish from the German environmental specimen bank. <u>Environmental Pollution</u> **216**: 866-876.

Gardner, M., Comber, S., Scrimshaw, M., Cartmell, E., Lester, J. and Ellor, B. 2012. The significance of hazardous chemicals in wastewater treatment works effluents. Science of Total Environment, 437, 363-372.

Gardner, M., Jones, V., Comber, S., Scrimshaw, M., Garcia, T., Cartmell, E., Lester, J. and Ellor, B. 2013. Performance of UK wastewater treatment works with respect to trace contaminants. Science of Total Environment, vol. 456-457, 359-369. http://www.sciencedirect.com/science/article/pii/S0048969713003938

Gardner, M., Jones, V. and Thornton, A., 2014. Chemical Investigations Programme: Volume 1 – Main Report. UKWIR Report Ref No. 13/EQ/01/6

Grinten, E. van der, et al.(2016). Milieuafwegingen in de geneesmiddelvoorziening RIVM Briefrapport 2016-0207. Rijksinstituut voor Volksgezondheid en Milieu

Gustavsson, M., Kreuger, J., Bundschuh, M., Backhaus, T., 2017. Pesticide mixtures in Swedish streams: Environmental risk, contribution of individual compounds and consequences of single-substance oriented risk mitigation. Sc. Tot. Env. 598, 973–983.

Johnson, A.C, Donnachie, R.L, Sumpter, J.P., Jürgens, M.D., Moeckel, C., Pereira, M.G. (2017). An alternative approach to risk rank chemicals on the threat they pose to the aquatic environment. Sc. Tot. Env., 599–600, 1372-1381.

JRC (Joint Research Centre), 2016. Second Review of the Priority Substances List under the Water Framework Directive: Monitoring-based exercise, Ispra (unpublished).

JRC (Joint Research Centre), 2017. Review of the 1st Watch List under the Water Framework Directive and Recommendations for the 2nd Watch List. (Authors: Loos, R., Marinov, D., Napierska, D., Sanseverino, I. Lettieri, T., Ispra.

Kienle, C., Gauch, R., Werner, I., Häner, A., 2015. Methoden zur Beurteilung der Wasserqualität anhand von ökotoxikologischen Biotests 41.

Kienzler, A., Bopp, S.K., van der Linden, S., Berggren, E., Worth, A. (2016). Regulatory assessment of chemical mixtures: Requirements, current approaches and future perspectives. 80, 321-334.

Knillmann, S., Orlinskiy, P., Kaske, O., Foit, K., Liess, M., 2018. Indication of pesticide effects and recolonization in streams. Sc. Tot. Env.630, 1619–1627.

König M., B.I. Escher, P.A. Neale, M. Krauss, K. Hilscherova, J. Novak, I. Teodorovic, T. Schulze, S. Seidensticker, M.A.K. Hashmi, J. Ahlheim, W. Brack 2017. Impact of untreated wastewater on a major European river evaluated with a combination of in vitro bioassays and chemical analysis. Environ. Pollut. 220: 1220-1230

Kunz, P.Y., Simon, E., Creusot, N., Sumith Jayasinghe, B., Kienle. C., Maletz, S., Schifferli, A., Schönlau, C., Aït-Aïssa, S., Denslow, N.D., Hollert, H., Werner, I., Vermeirssen, E.L.M. (2017). Effect-based tools for monitoring estrogenic mixtures: Evaluation of five in vitro bioassays. Water Research 110, 378-388

Langner, M., Junghans, M. et al., 2017. Hohe ökotoxikologische Risiken in Bächen. Aqua & Gas, No. 4, 58-68.

LAWA (Bund/Länder-Arbeitsgemeinschaft Wasser), 2015. "Mikroschadstoffe in Gewässern."

Leusch FDL, Neale PA, Arnal C, Aneck-Hahn NH, Balaguer P, Bruchet A, Escher BI, Esperanza M, Grimaldi M, Leroy G, Scheurer M, Schlichting R, Schriks M, Hebert A. Analysis of endocrine activity in drinking water, surface water and treated wastewater from six countries. Water Res. 2018 Aug 1;139:10-18. doi: 10.1016/j.watres.2018.03.056.

Lewis, K.A., Tzilivakis, J., Warner, D. and Green, A. (2016). An international database for pesticide risk assessments and management. Human and Ecological Risk Assessment: An International Journal, 22(4), 1050-1064. http://dx.doi.org/10.1080/10807039.2015.1133242.

Liess, M., Schulz, R., Liess, H.-D., Rother, B., Kreuzig, R., 1999: Determination of Insecticide Contamination in Agricultural Headwater Streams. Wat. Res. Vol. 33, No. 1, 239-247.

Liess, M., Von der Ohe, P.C., 2005. Analysing effects of pesticides on invertebrate communities in streams. Env. Tox. Chem., Vol. 24, No. 4, 954-965.

Loos, R., Carvalho, R., Antonio, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R.H., Schwesig, D., Gawlik, B.M., 2013. EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Res. 47, 6475e6487. http://dx.doi.org/10.1016/j.watres.2013.08.024.

Loos R., Gawlik BM, Locoro G, Rimaviciute E, Contini S, Bidoglio G. 2009 EU-wide survey of polar organic persistent pollutants in European river waters. Environ Pollut. 2009 Feb;157(2):561-8. doi: 10.1016/j.envpol.2008.09.020. Epub 2008 Oct 26.

Lyons et al. 2017. https://doi.org/10.1016/j.marenvres.2015.12.010

Malaj E, et al. (2014) Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc Natl Acad Sci USA 111(26):9549–9554

Mao, Z., Zheng, X.-F., Zhang, Y.-Q., Li, Y. and Wang, W. 2012. "Occurrence and Biodegradation of Nonylphenol in the Environment." Int. J, Mol. Sci 13(1) 491-505 doi: 10.3390/ijms13010491

Moschet, C.; Wittmer, I.; Simovic, J.; Junghans, M.; Piazzoli, A.; Singer, H.; Stamm, C.; Leu, C.; Hollender, J. How a complete pesticide screening changes the assessment of surface water quality. Environ. Sci. Technol. 2014, 48 (10), 5423–5432.

MSC-E, 2016. website http://www.msceast.org/index.php/pollution-assessment/and-more.

Muschket, M., Di Paolo, C., Tindall, A.J., Touak, G., Phan, A., Krauss, M., Kirchner, K., Seiler, T.-B., Hollert, H., Brack, W. (2018). Identification of Unknown Antiandrogenic Compounds in Surface Waters by Effect-Directed Analysis (EDA) Using a Parallel Fractionation Approach. Environ. Sci. Technol. 2018, 52, 288–297

Neale et al. 2017. Integrating chemical analysis and bioanalysis to evaluate the contribution of wastewater effluent on the micropollutant burden in small streams. Sci. Total Environ. 576: 785-795

North, K.D. (2004). Tracking Polybrominated Diphenyl Ether Releases in a Wastewater Treatment Plant Effluent, Palo Alto, California. Environ. Sci. Technol., 2004, 38 (17), pp 4484–4488. DOI: 10.1021/es049627y

Ogul (2015) ref required Ingo

Pirrone, N., S. Cinnirella, X. Feng, R. B. Finkelman, H. R. Friedli, J. Leaner, R. Mason, A. B. Mukherjee, G. B. Stracher, D. G. Streets and K. Telmer (2010). Global Mercury Emissions to the Atmosphere from Anthropogenic and Natural Sources. Atmos. Chem. Phys. 10, no. 13 (2010): 5951-64.

Posthuma, Leo, Brown, Colin David, Dyer, Scott et al. (2017) Prospective mixture risk assessment and management prioritizations for river catchments with diverse land uses. Environmental Toxicology and Chemistry. ISSN 1552-8618

Reemtsma, T., Berger, U., Arp, H.P.H., Gallard, H., Knepper, T.P., Neumann, M., Quintana, J.B., de Voogt, P., (2016): Mind the gap: persistent and mobile organic compounds—water contaminants that slip through. *Environ. Sci. Technol.* **50** (19):10308-10315

Ricklund, N., Kierkegaard, A., McLachlan, M.S. (2010). Levels and Potential Sources of Decabromodiphenyl Ethane (DBDPE) and Decabromodiphenyl Ether (DecaBDE) in Lake and Marine Sediments in Sweden. Environ. Sci. Technol., 44 (6), pp 1987–1991. DOI: 10.1021/es903701q

Rico et al. 2016. Relative influence of chemical and non-chemical stressors ... Sci Tot Environ 571: 1370-1382.

Roovaart, J. van den, Duijnhoven, N. van, Fribourg-Blanc, B., Siauve, S. and Prchalova, H. 2017. Emissions of pollutants to Europe's waters – sources, pathways and trends. ETC-ICM Technical report 3/2017

Roovaart, J. van den, Duijnhoven, N. van, Knecht, M., Theloke, J., Coenen P., Broeke, H. ten, 2013a. Diffuse water emissions in E-PRTR, Project report. Report 1205118-000-ZWS-0016, Deltares. Reference: ENV.C.3/SER/2011/0023

Roovaart, J. van den, Duijnhoven, N. van, Knecht, M., Theloke, J., Coenen P., Broeke, H. ten 2013b. Diffuse water emissions in E-PRTR, Dissemination document. Report 1205118-000-ZWS-0018, Deltares. Reference: ENV.C.3/SER/2011/0023

Samverkan, Vattenmyndigheterna i. "Del 2, Vattenförvalting 2009-2015 - Resultat Och Samverkan." Länsstyrelsen Västra Götalands län.

Schäfer et al. 2016. Contribution of organic toxicants to multiple stress in river ecosystems. Freshwater Biology 61:2116-2128

Schulz, F., Hahn, S., Rüdel, H., Uhlig, S., Hettwer, K., Kaltenbach, H.-M., 2015. Integrated assessment of mercury on the basis of surveys of the German Environmental Specimen Bank (ESB) (in German with a 16-pages English summary).

https://www.umweltprobenbank.de/upb_static/fck/download/Endbericht_Integrierte_Bewertung_Hg_2015_08_10_Web.pdf (6.8.2018)

Schulze et al. 2017. Assessment of a novel device for onsite integrative large-volume solid phase extraction of water samples to enable a comprehensive chemical and effect-based analysis. Science of The Total Environment: 581–582: 350-358

Shardlow, M., 2017. Neonicotinoid insecticides in British freshwaters.. 2016 Water Framework Directive Watch List Monitoring Results and Recommendations. Buglife. https://www.buglife.org.uk/news-and-events/news/heavy-neonicotinoid-insecticide-contamination-damaging-british-rivers (30.06.2018)

Thomas L. ter Laak, Rosa M.A. Sjerps & Stefan Kools. "Classifying Persistent Mobile Organic Compounds." Ministry of infrastructure and the Environment Netherlands, Watercycle Research Institute, 2015.

UBA (German Environment Agency), 2011 and 2016. Factsheets for RBSP regulated in German Surface Water Ordinance.

UBA (German Environment Agency), 2018. Recommendations for reducing micropollutants in waters. Dessau.

van den Berg, M. et al. 2006: The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. Toxicological Sciences, 93, 2, 223–241 https://doi.org/10.1093/toxsci/kfl055

van der Oost et al. 2017. SIMONI (smart integrated monitoring) as a novel bioanalytical strategy for water quality assessment: Part i-model design and effect-based trigger values. Environ Toxicol Chem. 36(9):2385-2399. doi: 10.1002/etc.3836.

Vorkamp, Katrin; Sanderson, Hans "European Environmental Quality Standards (EQS) Variability Study Analysis of the Variability between National EQS Values across Europe for Selected Water Framework Directive River Basin-Specific Pollutants." In Scientific Report No 198: Danish Centre for Environment and Energy, 2016.

Wernersson et al. 2015. The European technical report on aquatic effect-based monitoring tools under the water framework directive. Environmental Sciences Europe. 27:7 https://doi.org/10.1186/s12302-015-0039-4

Zhang,Bu Zhao, B., Mengqi Yu and Jianbo Zhang (2017). Emission inventory and environmental distribution of decabromodiphenyl ether in China. Sc. Tot. Env., 599–600, p. 1073-1081

7. Annex A: Derivation of emissions data for figures in chapter 2

The emission data for the priority substances were calculated as described below.

Data reported for the E-PRTR Regulation on industrial wastewater (P10) and UWWTPs (P8) are included in Figures 3.1-3.13. E-PRTR uses capacity thresholds (i.e. >100.000 p.e. for UWWTP and pollutant thresholds that vary per pollutant.

The datasource used was database version 11 (EEA, 2017a). To get an indication about possible trends in time, two years were considered: 2010 and 2015. Because data were not necessarily availabile for each year, the following selection process was applied. For 2010, data from 2010 were selected, then from 2011 if data from 2010 not available and then from 2009 if data from 2011 not available. In the case that no data were reported for 2009-2011, then no data were recorded for that substance by that country. Similarly, for 2015 data, 2015 was the preferred dataset, then 2014. If no data was reported for 2015 or 2014, no data was recorded for that country.

Data are included from the Water Information System Europe State of Environment (WISE SoE) emissions dataset. Industry (P10), UWWTPs (P8) and diffuse sources (other pathways) were used, from Waterbase_2015_v1_WISE1 (EEA, 2015b). Emissions data for 2010 were selected in similar way to E-PRTR data (i.e. from 2009-11 datasets). 2014 data were used as the latest available, 2013 data were used if 2014 data were not available.

WFD emission data for the year 2010 are included for Member States that reported via the WFD input inventory (EEA, 2017b). In some cases MS used another year for reporting (sometimes 2009) or an average of a number of years (like 2008/2009/2010). In that case the closest year to 2010 or the reported average is used. Because this dataset contained a number of errors and inconsistent data, an update of this dataset is used for this report. Depending on the pollutant, only 3-13 Member States reported data for industry and UWWTPs. Diffuse sources were only reported by a few MS. Most MS only reported a subset of river basin districts in the country.

Diffuse loads to surface water were estimated for 2010 by Roovaart et al (2013a, 2013b) for all EU Member States for a number of pollutants. Loads are estimated for agriculture (P3, P4, P5), direct deposition to waters (P1), road transport (P6, P7), inland shipping (P12), not connected households (P9) and UWWTPs not in E-PRTR < 100 000 pe (part of P8). Per pollutant, the load for these sectors is estimated, so it does not represent the total load of all existing diffuse sources.

The WFD dataset contains a number of double counting, inconsistencies and incorrect values, which makes it hard to interpret the data;

- Different years are used by the Member States for the different reporting streams and different reported data on the same sources appear to be inconsistent with each other;
- Different definitions about diffuse sources are used by the Member States.

In this context, numbers in the emissions tables and figures should be understood to be of low confidence. The loads given in the tables from different data sources cannot be summed, as there may be double counting.

Emissions data tables

Table A1: Existing emission and deposition data for mercury (t/a), in brackets: number of EU Member States reporting

Emissions to water	Mercury			
(t/a)	2005	2010	2014/2015	
Industry				
E-PRTR		2.6 (22*)	1.5 (23*)	
WISE		4.5 (22*)	2 (23*4)	
WFD		3.4 (13)		
UWWTP				
E-PRTR		1.7 (24*)	2.1 (21*)	
WISE		2.0 (23)	4 (20 ⁴)	
WFD		4.1 (10)		
Diffuse sources				
WISE		1.18 (2)	1.14 (1)	
WFD		0.7 (8)		
Study ¹		11 (28)		

^{*} including Norway

¹ Roovaart et al (2013b)

² EMEP (2017)

³ MSC-E (2016)

 $^{^4}$ Reported emissions to water in WISE (2014/2015) show extreme loads from a single member State, both for industry (85 t by one MS and 2 t by the other 23 MS reporting) and UWWTPs (1309 t by one MS and 4 t by the other 20 MS reporting). These values were excluded from calculation.

Table A2: Existing emission data for Benzo(g,h,i)-perylene, Indeno(123cd)-pyrene, Fluoranthene and Benzo(a)pyrene (t/a), in brackets: number of EU Member States reporting

Emissions to								
water	Benzo(g,h,i)-perylene	Indeno(123	Bcd)-pyrene	Fluora	nthene	Benzo(a)pyrene
(t/a)	2010	2014/2015	2010	2014/2015	2010	2014/2015	2010	2014/2015
Industry								
E-PRTR	0.1 (9*)	0.2 (7*)			7.3 (13*)	1.2 (11*)		
WISE	0.008 (4)	0.016 (3)	0.007 (3)	0.004 (2)	7.3 (14*)	151 (13*)	0.007 (3)	0.005 (2)
WFD	0.1 (4)		0.04 (5)		0.45 (7)		0.25 (7)	
UWWTP								
E-PRTR	0.1 (7)	0.04 (4)			0.1 (11)	0.1 (10)		
WISE	0.001 (1)	0.048 (2)		0.102 (1)	0.1 (11)	120 (7)	0.001 (1)	0.084 (1)
WFD	0.31 (2)		0.24 (2)		4.4 (5)		0.29 (4)	
Diffuse								
sources								
WISE	0.22 (2)	0.21 (1)	0.23 (2)	0.17 (1)	0.9 (2)	0.33 (1)	0.25 (2)	0.2 (1)
WFD	0.08 (2)		0.07 (3)		0.88 (6)		0.21 (5)	
Study ¹					0.97 (29*)			

^{*} including Norway

Table A2 (cont.): Existing emission data for Benzo(b)fluoranthene, Benzo(k)fluoranthene and Anthracene (t/a), in brackets: number of EU Member States reporting

Emissions to water	Benzo(b) f	luoranthene	Benzo(k) f	luoranthene	Anth	racene
(t/a)	2010	2014/2015	2010	2014/2015	2010	2014/2015
Industry						
E-PRTR					0.2 (6*)	0.2 (7*)
WISE	0.012 (4)	0.006 (2)	0.007 (3)	0.003 (2)	0.2 (9*)	0.2 (4*)
WFD	0.24 (5)		0.03 (5)		0.1 (6)	
UWWTP						
E-PRTR					0.1 (7)	1.7 (4)
WISE	0.002 (1)	0.071 (1)	0.001 (1)	0.087 (1)	0.1 (9)	0.3 (6)
WFD	0.26 (2)		0.2 (2)		0.34 (7)	
Diffuse sources						
WISE	0.5 (2)	0.3 (1)	0.22 (2)	0.15 (1)	0.23 (2)	0.08 (1)
WFD	0.15 (3)		0.07 (3)		1.2 (7)	
Study ¹					0.23 (29*)	

^{*} including Norway

Table A3: Existing emission data for brominated diphenylethers (t/a), in brackets: number of EU Member States reporting

¹ Roovaart et al (2013b)

¹ Roovaart et al (2013b)

Emissions to water	Brominated diphenylethers		
(t/a)	2010	2014/2015	
Industry			
E-PRTR	0.011 (2)	0.003 (2)	
WISE			
WFD	0.15 (3)		
UWWTP			
E-PRTR	0.03 (3)		
WISE	0.008 (1)		
WFD	0.004 (3)		
Diffuse sources			
WISE	0.01 (1)		
WFD	0.02 (4)		

Table A4: Existing emission data for DEHP (t/a), in brackets: number of EU Member States reporting

Emissions to water	DEHP		
(t/a)	2010	2014/2015	
Industry			
E-PRTR	0.5 (12)	0.4 (12*)	
WISE	3.7 (14)	2.5 (13)	
WFD	11 (6)		
UWWTP			
E-PRTR	27 (17*)	17 (16*)	
WISE	29 (17*)	28 (17*)	
WFD	17 (8)		
Diffuse sources			
WISE	0.11 (2)		
WFD	27 (5)		

Table A5: Existing emission data for 4-Nonylphenol (t/a), in brackets: number of EU Member States reporting

Emissions to water	4-Nonylphenol		
(t/a)	2010	2014/2015	
Industry			
E-PRTR	2.9 (11)	4.5 (10*)	
WISE	3.5 (11)	7.3 (12*)	
WFD	1.3 (4)		
UWWTP			

E-PRTR	35 (16*)	23 (15*)
WISE	24 (16*)	22 (16*)
WFD	1.1 (6)	
Diffuse sources		
WISE		
WFD	2.2 (5)	

^{*} including Norway

Table A6: Existing emission data for Cadmium, Nickel and Lead (t/a), in brackets: number of EU Member States reporting

Emissions to water	Cad	lmium	Ni	ckel	Lo	ead
(t/a)	2010	2014/2015	2010	2014/2015	2010	2014/2015
Industry						
E-PRTR	7.2 (21*)	8.7 (20*)	120 (24*)	96 (26*)	110 (26*)	68 (22*)
WISE	8.9 (24*)	53 (23*)	142 (26*)	186 (26*)	134 (26*)	101 (27*)
WFD	18 (13)		77 (13)		46 (13)	
UWWTP						
E-PRTR	11 (21*)	8.8 (22*)	179 (24*)	165 (24*)	69 (22*)	68 (24*)
WISE	14 (22*)	60 (25*)	217 (25*)	227 (25*)	103 (22*)	88 (26*)
WFD	12 (13)		121 (12)		51 (11)	
Diffuse sources						
WISE	2.02 (2)	0.76 (1)	62 (2)	7 (1)	52 (2)	31 (1)
WFD	2.1 (8)		116 (9)		77 (9)	
Study ¹	50 (28*)		473 (28*)		462 (28*)	

Table A7: Existing emission data for Hexachlorocyclohexane (tt/a), in brackets: number of EU Member States reporting

Emissions to water	Hexachlorocyclo- hexane		
(t/a)	2010	2014/2015	
Industry			
E-PRTR	0.4 (6)	0.03 (2)	
WISE			
WFD	0.001 (5)		
UWWTP			
E-PRTR	0.1 (4)	0.01 (3)	
WISE	0.02 (1)		
WFD	1.2 (4)		
Diffuse sources			
WISE	0.02 (1)		

^{*} including Norway

1 Roovaart et al (2013)

WFD	0.06 (3)	
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Table A8: Existing emission data for Isoproturon (t/a), in brackets: number of EU Member States reporting

Emissions	to water	Isoproturon	
(t,	/a)	2010	2014/2015
Industry			
	E-PRTR	0.08 (6*)	0.04 (2)
	WISE	0.08 (2)	0.0002 (1)
	WFD	0.03 (5)	
UWWTP			
	E-PRTR	0.2 (8)	0.1 (6)
	WISE	0.006 (1)	0.00001 (1)
	WFD	0.49 (3)	
Diffuse so	urces		
	WISE	6.8 (2)	0.1 (1)
	WFD	13 (5)	

^{*} including Norway

Table A9: Existing emission data for Tributyltin-cation (t/a), in brackets: number of EU Member States reporting

Emissio	ns to water	Tributyltin-cation	
	(t/a)	2010	2014/2015
Industry	,		
	E-PRTR	40 (5)	0.004 (2)
	WISE		0.0005 (2)
	WFD	0.01 (4)	
UWWTP	1		
	E-PRTR	0.1(7)	0.01(3)
	WISE		0.002 (2)
	WFD	0.02 (3)	
Diffuse	sources		
	WISE		
	WFD	0.02 (2)	