Hazardous substances in Europe's fresh and marine waters

An overview

European Environment Agency

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Acknowledgements

Executive summary

Chemicals are an essential part of our daily lives. They are used to produce consumer goods, to protect or restore our health and to boost food production, to name but a few examples — and they are also involved in a growing range of environmental technologies. Europe's chemical and associated industries have developed rapidly in recent decades, making a significant contribution to Europe's economy and to the global trade in chemicals.

Whilst synthetic chemicals clearly bring important benefits to society, some of them are hazardous, raising concerns for human health and the environment depending on their pattern of use and the potential for exposure. Certain types of naturally occurring chemicals, such as metals, can also be hazardous. Emissions of hazardous substances to the environment can occur at every stage of their life cycle, from production, processing, manufacturing and use in downstream production sectors or by the general public to their eventual disposal. Emissions arise from a wide range of land-based and marine sources, including agriculture and aquaculture, industry, oil exploration and mining, transport, shipping and waste disposal, as well as our own homes. In addition, concern regarding chemical contamination arising from the exploitation of shale gas has grown recently.

Hazardous substances in water affect aquatic life…

Hazardous substances are emitted to water bodies both directly and indirectly through a range of diffuse and point source pathways. The presence of hazardous substances in fresh and marine waters and associated biota and sediment is documented by various information sources, including national monitoring programmes, monitoring initiatives undertaken by the Joint Research Centre (JRC), reporting under the Water Framework Directive (WFD), international marine conventions (e.g. HELCOM and OSPAR) and European research studies. These substances comprise a wide range of industrial and household chemicals, metals, pesticides and pharmaceuticals.

Hazardous substances can have detrimental effects on aquatic biota at molecular, cellular, tissue, organ and ecosystem level. Substances with endocrine-disrupting properties, for example, have

been shown to impair reproduction in fish and shellfish in Europe, raising concerns for fertility and population survival. The impact of organochlorines upon sea birds and marine mammals is also well documented, as is the toxicity of metals and pesticides to freshwater biota. From a socio-economic point of view, such impacts diminish the services provided by aquatic ecosystems, and consequently the revenue that can be derived from them.

…and can pose risks to human health

Human exposure to man-made chemicals has been implicated in a range of chronic diseases, including cancer as well as reproductive and developmental impairment. Exposure to toxic chemicals can occur via inhalation, ingestion and direct contact with skin, although the understanding of the relative risk posed by each of these exposure routes remains incomplete. However, exposure can be linked to the presence of hazardous substances in water, through the ingestion of contaminated drinking water and the consumption of contaminated freshwater fish and seafood. The exceedance of regulatory levels in seafood is documented for several hazardous substances in the seas around Europe. In addition, whilst human exposure to mercury in the Arctic, in part through the consumption of marine food, has declined, concentrations in the blood of more than 75 % of women sampled in Greenland exceed US guideline levels.

Alongside concerns about exposure to individual substances, awareness is growing with regard to the importance of mixtures of several chemicals, as found in the more polluted water bodies of Europe. Laboratory studies have shown that the combined effects of chemicals upon aquatic life can be additive — resulting in observable detrimental effects for combinations of chemicals even if these are present, individually, at levels below which any adverse effects can be detected. Such concerns also extend to potential effects arising from human exposure to a mixture of chemicals via various pathways, including water. Biological effects-directed measurements have proved to be effective in addressing the problems of complex chemical mixtures in European water bodies.

In addition to the potential for adverse impacts upon human and ecosystem health, the presence of

hazardous substances in drinking water supplies requires their removal. Alternatively, where the level of treatment involved is so high as to be uneconomic, a supply can be decommissioned. In both cases, significant costs are incurred. A key measure for reducing the level of purification required for Europe's drinking water is the establishment of safeguard or protection zones around the source. The creation of such zones, recognised in the WFD legislation, must be associated with regulatory powers to control polluting activities.

Legislation designed to protect Europe's waters…

The implementation of more established legislation related to chemicals has produced positive outcomes. Abatement measures established under the Integrated Pollution Prevention and Control (IPPC) Directive, for example, have contributed to a decline in metal emissions to water and air, whilst legislation relating to the production, use and disposal of polychlorinated biphenyls (PCBs) has resulted in declines in concentrations found in marine biota. A similar outcome has resulted from the banning of tributyltin (TBT) in anti-fouling paints due to its endocrine-disrupting impacts on marine invertebrates, although high levels in marine sediments can still be observed in certain locations.

Europe has also introduced a range of relatively recent legislation to address the use of chemicals and their emissions to the environment, including water. The Regulation on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), designed to improve the protection of human health and the environment from the risks posed by chemicals, has a key role to play in this respect. REACH attributes greater responsibility to industry with regard to managing these risks and providing safety information on substances used. The Regulation also calls for the progressive substitution of the most dangerous chemicals once suitable alternatives have been identified.

The chemical quality of Europe's surface waters is primarily addressed by the recently adopted Environmental Quality Standards Directive (EQSD). This WFD 'daughter' directive defines concentration limits for pollutants of EU-wide relevance known as priority substances (PSs). The limits are defined both in terms of annual average and maximum allowable concentrations, with the former protecting against long-term chronic pollution problems and the latter against short-term acute pollution. Some of these pollutants have been designated as priority hazardous substances (PHSs) due to their toxicity, their persistence in the environment and their bioaccumulation in plant and animal tissues. The EQSD requires cessation or phase-out of discharges, emissions and losses of PHSs. For any substance identified as being of concern at local, river basin or national level, but not as a PS or PHS at EU level, standards have to be set at national level. Compliance with this requirement is critical.

…is facing new challenges

Some recent information with respect to the chemical status of Europe's surface water bodies is available within the WFD river basin management plans (RBMPs) which indicate, in general terms, that a variety of hazardous substances pose a threat to good chemical status in Europe. These include certain substances, for example mercury, TBT and polyaromatic hydrocarbons (PAHs), which can be described as persistent, bioaccumulative and toxic and which occur widely in the environment. Although regulation has led to documented reductions in the emissions of such substances to air and water (indeed, the presence of many is a legacy of past use), their persistence and ubiquity, particularly in sediment and biota, mean that they continue to pose a risk to aquatic environments even at sites far from human activity. The presence of these substances can cause widespread failure to achieve good chemical status under the WFD despite, in some cases, the absence of any significant risk from other types of substances.

Some hazardous substances are hydrophobic and tend to accumulate in sediment and biota, with the result that their concentrations in these matrices are likely to be higher and, therefore, more detectable and measurable than in water. If measurements are made in the water column, the risk to the aquatic environment may be underestimated, and if different matrices are used in different locations and across different Member States, the results may not be directly comparable. A harmonisation at EU level is, therefore, desirable.

For some pollutants, awareness and a currently incomplete understanding of potential effects have developed only recently. These emerging pollutants include substances that have existed for some time, such as pharmaceuticals and personal care products, but also relatively new substances, such as nanomaterials. Their inclusion in routine monitoring programmes has so far been limited, making it difficult to robustly assess the risks to the environment and human health, and thus to

justify regulation and better monitoring. Targeted monitoring of selected emerging pollutants across the EU would be desirable to ensure timely awareness of potentially problematic substances that might need to be regulated. This monitoring should be supported by European research studies.

The question of hazardous substances in Europe's fresh and marine waters is a complex issue, and climate change will add a further layer of complexity. In the absence of appropriately strong measures, this phenomenon is likely to adversely affect chemical water quality over the coming decades. In regions where more intense rainfall is expected, the frequency and severity of polluted urban storm flows is predicted to increase, whilst the flushing to water of agricultural pollutants, including pesticides and veterinary medicines, may be exacerbated. Hotter, drier summers and increasingly severe and frequent droughts will deplete river flows, reducing contaminant dilution capacity and leading to elevated concentrations of hazardous substances. Rising water temperatures and other stressors associated with climate change may interact with hazardous substances to impact the immune system health of aquatic organisms. Ocean acidification, driven by increasing atmospheric carbon dioxide (CO_2), may change the speciation of metals in seawater and, therefore, their interaction with marine organisms. In addition, coastal erosion — likely to be intensified by climate change — may lead to the exposure of historical landfill sites along the coastlines of Europe, releasing hazardous substances to coastal waters.

Effective measures exist…

A range of measures can be implemented to reduce the emission of hazardous substances to water. It encompasses product substitution, restrictions on marketing and use, requirements to demonstrate the implementation of clean production processes and best available techniques in applications for industrial permits, fiscal instruments, the setting of emissions and environmental quality standards, and action to raise public awareness.

Whilst controls 'at source' are desirable, it is very likely that other measures to attenuate the emission of hazardous substances to water will remain essential. Such measures include advanced wastewater treatment, urban stormwater controls and specific agri-environmental practices such as riparian buffer strips. Reducing emissions of hazardous substances has been shown to yield economic and societal benefits.

…but they rely on sound information

It is not practical or affordable to sample and analyse at sufficient spatial and temporal resolution for hundreds of individual chemicals within fresh and marine waters, including aquatic biota and sediments. However, the focus upon a few pre-selected priority substances bears a strong risk of missing other problematic substances. In addition, such an approach disregards the effects of chemical mixtures.

To address these issues, recent European research studies have led to the development and testing of new assessment and modelling tools that help to link chemical contamination with observed deterioration of ecological quality. Such tools include approaches to evaluate existing chemical and biological monitoring data, together with site-specific experimental techniques to establish cause-effect relationships. Further development of biological effects tools integrated with analytical chemistry is desirable and could contribute, in due course, to the identification of substances associated with risks, in the wider context of the update of the WFD Article 5 'pressures and impacts' analysis. European research funds can play an important role in the further development of these tools.

For many hazardous substances, information on industrial emissions to water must be reported under the European Pollutant Release and Transfer Register (E-PRTR). To date, however, reporting under E-PRTR is incomplete as to the spatial extent and temporal resolution of data describing emissions to water — markedly so, for some substances. It is important not only to overcome this limitation in the reporting, but also to improve the quantitative understanding of the sources, emissions and pathways of all hazardous substances significantly. Advances in this area will facilitate the identification of appropriate measures to address chemical pollution of aquatic environments.

Chemicals should be produced and used more sustainably

Despite the comprehensive suite of legislation now implemented throughout Europe, the ubiquitous use of chemicals in society and their continuous release represent a major challenge in terms of the protection of aquatic ecosystems and human health. Efforts to promote a more sustainable consumption and production of chemicals are needed. They are likely to require a mix of policy responses, including regulation, economic

incentives and information-based instruments. Implementing a more sustainable approach to the consumption and production of chemicals would not only benefit Europe's environment but also reduce the detrimental effects arising in other parts of the world as a result of the growing proportion of goods imported to Europe.

To help achieve a more sustainable production of chemicals, wider implementation of 'green chemistry' is required. This approach involves developing new processes and technologies that maintain the quality of a product but reduce or eliminate the use and generation of hazardous substances. The adoption of sustainable, green chemistry techniques has been shown to generate financial benefits and hence provide competitive advantage. Currently, however, there is no comprehensive EU legislation on sustainable chemistry in place.

1   Introduction

Chemical substances are an essential part of our daily lives. They are used in health and consumer products, in food production and in a growing range of environmental technologies, to name but a few examples. They can be natural substances, they can be formed as the unintended by-product of natural and human-induced processes, or they can be synthesised specifically for use in industrial processes and consumer products (OSPAR, 2009a). Tens of thousands of chemicals are available on the European market, with the European Union holding a substantial share of global exports and imports.

Whilst chemicals bring important benefits to society, some of them are hazardous, raising concerns for human health and the environment depending on their pattern of use and environmental exposures. Annual production of hazardous chemicals (i.e. toxic chemicals as defined by Eurostat) in the European

Union amounted to approximately 200 million tonnes in 2008 (Figure 1.1). Following several decades of substantial growth, it has tended to stabilise in recent years.

Hazardous substances are released to the wider environment via various pathways, with the potential for detrimental effects upon both terrestrial and aquatic ecosystems. Observations from aquatic ecosystems in the 1950s and 1960s were the first early warnings of the environmental dangers of the widespread production and use of industrial and man-made chemicals, including persistent organic pollutants (POPs). The concern that arose led to the implementation (in 1976) of the Dangerous Substances Directive (now integrated into the WFD) which aimed to eliminate pollution by a select list of substances and reduce the level of certain others. This directive, coupled with other international initiatives, led to the decline of certain substances,

Figure 1.1   Production of toxic chemicals in the EU

Production volumes of toxic chemicals in EU (27 countries)
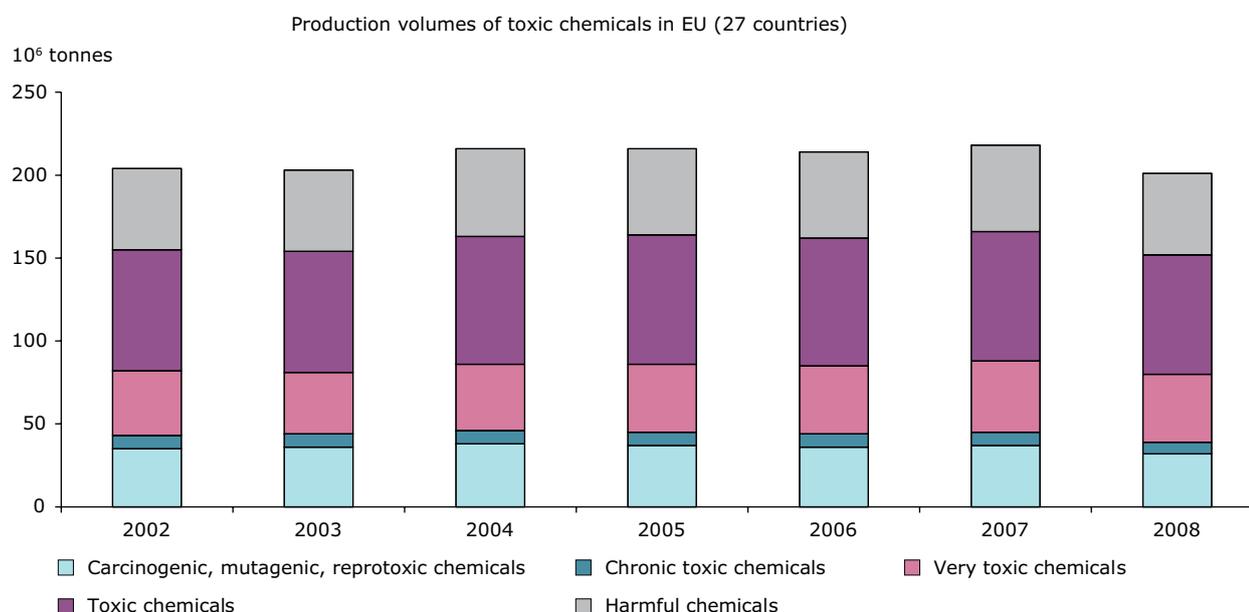
Note: The graph was compiled for 168 toxic chemicals based on production quantities collected pursuant to the Prodcom regulation (Council Regulation (EEC) 3924/91 on the establishment of a Community survey of industrial production). The toxicity classes were assigned according to the classification and labelling system ('risk phrases' or R-phrases) designated for the individual substances in Annex VI to the Dangerous Substances Directive as amended by EC Directive 2001/59/EC (adapting to technical progress for the 28th time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances).

Source: Eurostat.

including some metals and POPs, in aquatic environments (EEA, 2003).

In recent years, the body of information, derived from numerous sources, describing the presence of hazardous substances in Europe's fresh, estuarine, coastal and marine waters has grown. In addition to those substances of early concern, such as POPs, certain metals and pesticides, the presence of pharmaceuticals, personal care products, phenols and phthalates is documented. In some locations, these various substances are known to occur at a level sufficient to cause detrimental impacts upon aquatic biota. Such toxic impacts diminish the highly valuable services that can be derived from marine and freshwater ecosystems (Martinez et al., 2007). Aside from the effects upon aquatic biota, water is also a pathway by which humans can become exposed to hazardous substances — via drinking water supplies that have been inadequately treated, or through the consumption of contaminated freshwater fish and sea food.

A range of legislation and policy is now in force to address the use of hazardous substances, their release to Europe's environment, including its waters, and their levels within aquatic environments. Much of this legislation has been implemented relatively recently, including REACH and the WFD, although some, such as the IPPC Directive and its regulation of industrial emissions, is more established.

In addition to the significant legislative developments of recent years, a rapidly expanding body of information is available with respect to the presence and toxic impacts of hazardous substances in Europe's fresh and marine waters. Typically, however, this information is fragmented in nature, and any individual sources of information tend to focus on specific aspects, for example, a particular geographical region, a distinct chemical group, or a single organism of concern. The objective of this report, therefore, is to address this limitation and provide a broad, integrated and up-to-date overview of the issue of hazardous substances in Europe's water. More specifically, this report aims to:

- document the sources, pathways, emissions and discharges of selected hazardous substances to Europe's fresh and marine waters (Chapter 2);

- provide an overview of the current status of, and recent trends in, chemical pollution of Europe's fresh and marine waters using information from a variety of sources, including reporting under the WFD, the EEA's Eionet-Water database and monitoring programmes conducted by the JRC and regional sea conventions (Chapter 3);

- describe some of the impacts that hazardous substances can have upon aquatic biota and outline the potential for human exposure to these substances via water (Chapter 4);

- outline key European policy and legislation that addresses the use of hazardous substances and their release to water (Chapter 5);

- highlight selected measures to reduce the emissions of hazardous substances to water (Chapter 5);

- present tools and innovative approaches to assess the sources, levels and effects of hazardous substances, including chemical mixtures (Chapter 6);

- provide a supporting background document for the various chemicals-related parts of the EEA's forthcoming 2012 'State of Europe's water' reporting, to be undertaken in conjunction with the European Commission.

The term 'hazardous substances' is, by necessity, used in a broad sense throughout this report, encompassing substances of very high concern as defined by REACH, hazardous substances as defined by OSPAR, the PSs, PHSs and Annex VIII pollutants identified by the WFD, and a number of the substances subject to E-PRTR reporting. In addition, the use of the term includes the potentially wide-ranging list of substances for which Member States are to establish their own surface and groundwater standards. It is important to note that designation and classification under this suite of legislation is ongoing, as are the authorisation of substances under REACH and the designation of PS under the EQSD. The report also refers to 'emerging pollutants', i.e. those for which the potential for adverse effects has only recently become apparent and for which the understanding of such effects is currently incomplete.

2 Sources, pathways and emissions

2.1 Introduction

Emissions and releases of hazardous substances can occur at all stages of their life-cycle, from production, processing, manufacturing and use in downstream production sectors and by the general public to the eventual disposal of these substances. This chapter provides an overview of the key sources of hazardous substances and of the pathways by which these substances are emitted to both fresh and marine waters.

In addition, a series of case studies examines five selected hazardous substances (or groups of substances) to illustrate the diversity of patterns of emissions, pathways and environmental fate. These include metals for which environmental toxicity has long been understood, emerging pollutants for which the potential for detrimental effects has only recently become apparent, and ubiquitous substances that are transported over long distances in the atmosphere. Another subsection focuses on a heterogeneous group of substances that cause a particular detrimental effect in aquatic biota — the phenomenon of endocrine disruption.

2.2 Urban environment

Hazardous substances arise from various sources in the urban environment. These include household chemicals such as personal care products and medicines, a wide range of industrial chemicals, substances such as hydrocarbons and heavy metals released by the transport sector, building and construction materials, and pesticides used to control unwanted plant growth on sports grounds and buildings, in public parks and private gardens, and on roads and railways.

Certain hazardous substances are released to air from industrial and waste facilities and vehicle emissions. Subsequently, their deposition to water bodies can occur both directly and indirectly, for example via soil and urban drainage systems. In some cases deposition may occur close to the point of emission, although some hazardous substances, such as mercury and persistent organic pollutants, are known to be subject to long-range transboundary atmospheric transport. As a consequence, they can adversely affect aquatic

environments in remote regions such as the Arctic. Addressing their impacts requires political initiative at the regional and the global scale.

Household wastewater in Europe is predominantly collected by a sewer network and directed to municipal wastewater treatment plants. Industrial wastewaters are also typically treated, either on-site or by transfer to a municipal plant. Other urban pollutants, however, particularly those deposited from the atmosphere or released from vehicles (e.g. from wear on brakes and tyres) are, originally at least, diffuse in nature, as they are washed from impervious areas by surface run-off. Their subsequent fate depends upon whether the run-off is collected and directed to a treatment plant or discharged untreated to a receiving water body.

Whilst household and industrial wastewater treatment has been implemented progressively across Europe, the process does not remove all hazardous substances, with household and industrial chemicals and pharmaceuticals, for example, being detected in treated effluent that is subsequently discharged to surface waters (Ashton et al., 2004; Gros et al., 2010; HELCOM, 2010; Miège et al., 2009; Reemtsma et al., 2006). Such discharges are near-continuous and hence these substances do not need to be persistent in nature to give rise to chronic effects in aquatic ecosystems. In addition, sewage sludge generated via municipal wastewater treatment can be contaminated by hazardous substances including pharmaceuticals (Giger et al., 2003) and personal care products (Brausch and Rand, 2011).

In many cities across Europe, the sewage collection system has also been designed to collect run-off from streets, roofs and other impervious surfaces. The collection pipes and treatment plants of such combined systems are designed to be able to handle both sewage and urban run-off generated during rain storms, but only up to a certain level. During larger storm events, the combined flow generated can exceed the capacity of the system. When this happens, relief structures are built into the collection system to prevent sewage back-up into streets and homes, enabling the flows to bypass the treatment plants and discharge the combined waste more or less untreated to a receiving watercourse. Such combined sewer overflows (CSOs), together with

discharges from separate stormwater systems, typically discharge a range of pollutants including hazardous substances (Chon et al., 2010; Gounou et al., 2011; Sally et al., 2011) and can cause rapid depletion of oxygen levels in receiving waters (Even et al., 2007). In addition, the quality of coastal waters near such discharges can deteriorate very quickly.

However, other than in respect of their design criteria, neither CSOs nor discharges from separate stormwater systems are subject to direct environmental regulation, and little information is publicly available describing their pollutant loads. Innovative solutions are required, particularly as the retro-separation of combined sewers is expensive and technically challenging. Good practice is already apparent in Europe in this respect, such as the retention of overflows in storage ponds during heavy rainfall, with a subsequent back-pumping to the system for treatment. In the Greater Paris region, for example, such stormwater retention ponds have contributed to a clear decline in sewer overflow volumes (Meybeck et al., 2007).

2.3   Agriculture

Pesticides used in agriculture are widely detected in freshwater, often transported by diffuse pathways via surface run-off and leaching. Point discharges of pesticides are also important, however, and occur through accidental spillage, sprayer loading and wash-down, and inappropriate storage and disposal. Just how much pesticide pollution of freshwater occurs depends on a range of factors including the chemical nature of the pesticide, the physical properties of the landscape, and weather conditions. Biocidal products are also used, for example to treat livestock and protect stores. Wash-off and accidental spillage may occur.

Metal emissions from agriculture include cadmium, found naturally in the phosphate rock used to make fertiliser, and zinc, an essential trace element that is added to animal feed. A significant proportion of zinc is not absorbed by livestock, however, and is excreted in manure that may then be flushed into rural streams. Copper, too, is found in feedstuffs and hence manure, but can also come from copper baths used in the treatment and disinfection of livestock hooves. While metals are generally well retained in soil, there is evidence that agricultural sources can make a significant contribution to freshwater loads (RIVM, 2008a and 2008b).

Veterinary medicinal products are found in manure and slurry, excreted directly by grazing livestock or spread on to land after a period of storage. Once on the land surface, they are susceptible to run-off into surface waters or infiltration to groundwaters.

2.4   Mining

Mining exerts a localised but significant pressure upon the chemical and ecological quality of water resources in parts of Europe, particularly with respect to the discharge of heavy metals. Abandoned mines represent a particular threat since, in the absence of continued pumping, groundwater levels rise and, ultimately, discharge contaminants within the mine workings. Mine discharges threaten the attainment of good water quality in a number of locations across Europe.

2.5   Landfills and contaminated land

Landfill sites can be a source of pollution to the aquatic environment. Precipitation percolates down through the waste, picking up a range of pollutants

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Box 2.1 Exploitation of shale gas

Concern with respect to chemical contamination associated with the exploitation of shale gas has recently gained in prominence throughout Europe. With conventional natural gas reserves declining globally, shale gas has emerged as a potentially significant new source of unconventional gas. Exploitation of shale gas has been advanced by developments in horizontal drilling and well stimulation technologies such as hydraulic fracturing (Wood et al., 2011). The exploitation process does, however, involve a strong risk of negative environmental impacts, including potential contamination of ground and surface water by chemicals used in the fracturing process and the mobilisation of sub-surface contaminants such as heavy metals and naturally occurring radioactive materials (Wood et al., 2011). In addition, methane contamination of drinking water has been associated with the process (Osborn et al., 2011). The information required to fully evaluate these risks is currently unavailable. Therefore, a precautionary approach should be adopted with respect to extraction in Europe.

including hazardous substances, whilst water is also released from the waste itself as it degrades (Slack et al., 2005). The leachate subsequently collects at the base of the landfill where it can, potentially, contaminate groundwater.

In modern landfills, leachate is collected by pipes and either treated on site, with the effluent discharged to a neighbouring watercourse, or transported to a sewage treatment plant for processing. Older landfills, however, do not incorporate such leachate collection or the use of an impermeable base liner. As a consequence, contaminated leachate is free to flow downwards unrestricted (Baun et al., 2004). In the European Union, the Landfill Directive specifies technical and engineering requirements for water control and leachate management. In addition, restrictions on hazardous waste apply.

Aside from landfill sites, land can be contaminated by a range of hazardous substances released from historical industrial activities or, more recently, from unintentional leaks and spills. Such substances can include solvents, oil, petrol, heavy metals and radioactive substances. Without appropriate remedial action, ground and surface waters can also be polluted.

2.6 Transport of hazardous substances to coastal waters

Once released to rivers, hazardous substances can be transported downstream and ultimately discharged to coastal waters, although numerous processes can occur 'in-stream' to attenuate this transport. Of particular note is the deposition of substances onto the river bed. Hazardous substances attached to other particles, such as organic material and eroded soil, are particularly susceptible to this sedimentation process and, once settled on the river bed, can pose a threat to benthic biota. During periods of higher river flow, however, bed sediments and their associated contaminants can be re-suspended into the water column and transported downstream until flow declines and sedimentation occurs once more.

This cycle of sedimentation and re-suspension means that, for a number of hazardous substances, the total load transported by the river can be markedly underestimated unless monitoring occurs during periods of high river flow. The proportion of a hazardous substance load that is ultimately discharged to coastal waters remains susceptible to sedimentation in estuarine and near coastal waters. Elevated levels of cadmium and mercury, for example, are observed in Baltic Sea sediments

(HELCOM, 2010). Re-suspension of hazardous substances in estuarine and coastal waters can then occur when sediments are disturbed and displaced, for example, through dredging (OSPAR, 2009a).

2.7 Sources emitted directly into the marine environment

In addition to the waterborne transport of substances emitted from land-based sources and deposition from the atmosphere, hazardous substances are also released directly into the marine environment. Shipping, harbour and port activities, offshore oil exploration and aquaculture all emit a variety of hazardous substances, whilst the discharge of sewage and industrial wastewater directly (i.e. not via rivers) into coastal waters can also occur.

Pollution from shipping, including oil and other hazardous substances, arises from accidents as well as operational and illegal discharges. Some evidence of decreasing oil pollution is apparent in the OSPAR region and can be attributed to the capture of technological advances (such as the phasing out of single-hull tankers) within international shipping regulations (OSPAR, 2009b).

Discharges of oil from offshore installations can occur from produced water, displacement water and accidental spillage, with flaring operations also playing a minor role. Produced and displacement water account for the largest amounts of oil discharged, with the exception of large, infrequent oil spills. Both have declined over recent years in the OSPAR region, a development which is attributable to the implementation of standards set with respect to discharge concentrations (OSPAR, 2009c).

In response to increased demand for fish products and the reduced supply of wild caught fish, a large increase in total European aquaculture production has been observed over the past 15 years (FAO, 2010). Today, EU and EFTA aquaculture produces about 1.8 million tonnes of fish, shellfish and crustaceans annually, generating a turnover of around EUR 3.2 billion while supporting 65 000 jobs (EEA, 2010a). Release to the marine environment of biocides, antibiotics and anti-fouling chemicals arises from the sector, particularly in connection with finfish production, although any related impacts are thought to be local and site-specific (OSPAR, 2009d). In recent years, the increased use of vaccines has reduced the use of antibiotics in the sector, whilst copper and (to a lesser extent) zinc have replaced TBT as anti-fouling agents.

2.8   Case studies

2.8.1   Mercury

Mercury and most of its compounds are extremely toxic to both humans (Grandjean et al., 2007) and the environment and, as a consequence, are classified as PHSs under the EQSD. Mercury is a persistent pollutant and subject to long-range transboundary transport that has contributed to the building of a global pool of mercury in the environment; about 40 % of annual mercury deposition to Europe originates from outside the continent (Travnikov, 2005).

Whilst concentrations of mercury in ambient air are generally too low to present a risk to human health (UNEP, 2008), concern over mercury in the atmosphere relates to the fact that, following deposition, it can be taken up by biota and subsequently enter the food chain; ingestion via seafood is a particular concern. The uptake in biota is facilitated by the conversion of inorganic mercury to organic methyl mercury. Methyl mercury is lipid soluble and 10 to 100 times more biologically

available than inorganic mercury. In the human body, it has a tendency to accumulate in the nerve tissue.

Methylation in the environment is effected by bacteria and other microorganisms in the soil and in lake and coastal sediments. Through this mechanism, historical deposition of mercury continues to affect biota. This explains why there is no obvious reduction in methyl mercury levels in lake fish in some areas of Europe (Scandinavia). Recent findings show that atmospheric mercury deposition to the sea is methylated by algae or bacteria in the surface film of the water. This is a likely reason for the surprisingly high concentrations of methyl mercury found in long-lived fish like tuna, swordfish and sharks.

In Europe, all mining of mercury has now ceased and the majority of production results from the recycling of products and wastes containing mercury. Mercury is used in the chloro-alkali industry, in electrical control and switching devices, measuring and control instruments, lighting, batteries and dental amalgams. Emissions

Map 2.1   Total (dry and wet) deposition of mercury across Europe, in 2008 (g/km²/year)
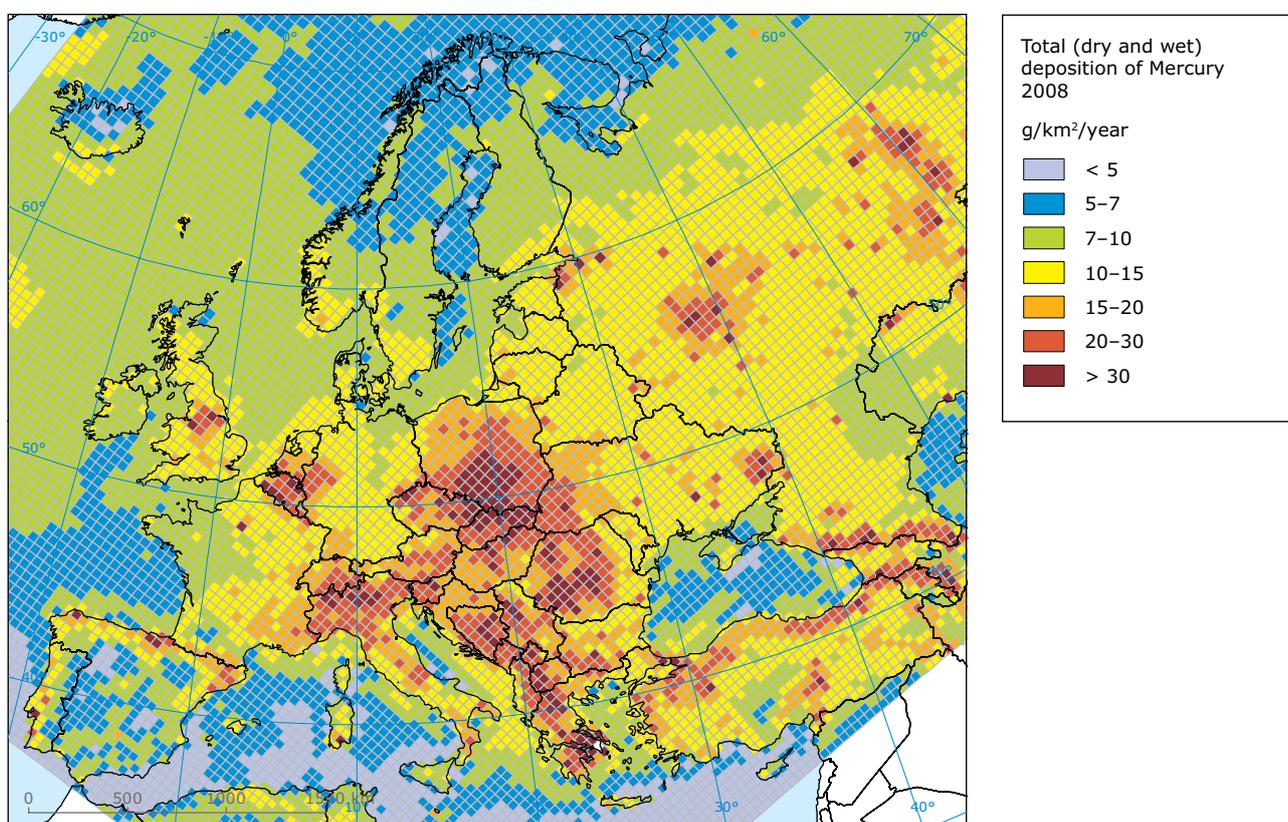
Source: European Monitoring and Evaluation Programme (EMEP).

of mercury to air in Europe arise predominantly from combustion facilities and from the metal and chemical industries.

According to reporting under E-PRTR, European emissions of mercury to air totalled 37.8 tonnes in 2008. The implementation of abatement technologies together with a general decline in the burning of coal (which contains mercury as a contaminant) have led to a decrease in emissions to air of 61 % across EEA member countries between 1990 and 2008. However, unless the abatement technologies now generally employed in Europe and North America are implemented in other parts of the world, global emissions (the largest share of which originates from the combustion of fossil

fuels) are predicted to increase by about 25 % by 2020 (Sundseth et al., 2010). Total deposition (wet and dry) of mercury currently varies widely across Europe, from less than 5 g/km^2/year to more than 30 g/km^2/year (Map 2.1).

Mercury emissions to water reported under E-PRTR totalled 6.6 tonnes in 2008 (Map 2.2), 'released' from 420 facilities. Much of this total (63 %) was released from urban wastewater treatment plants, whilst 16 % arose from chemical industrial facilities with on-site treatment.

However, Map 2.2 should not be viewed as representing total mercury emissions to water. Three other factors must be taken into account:

Map 2.2   Emissions of mercury to water based on E-PRTR reporting of 2008 data
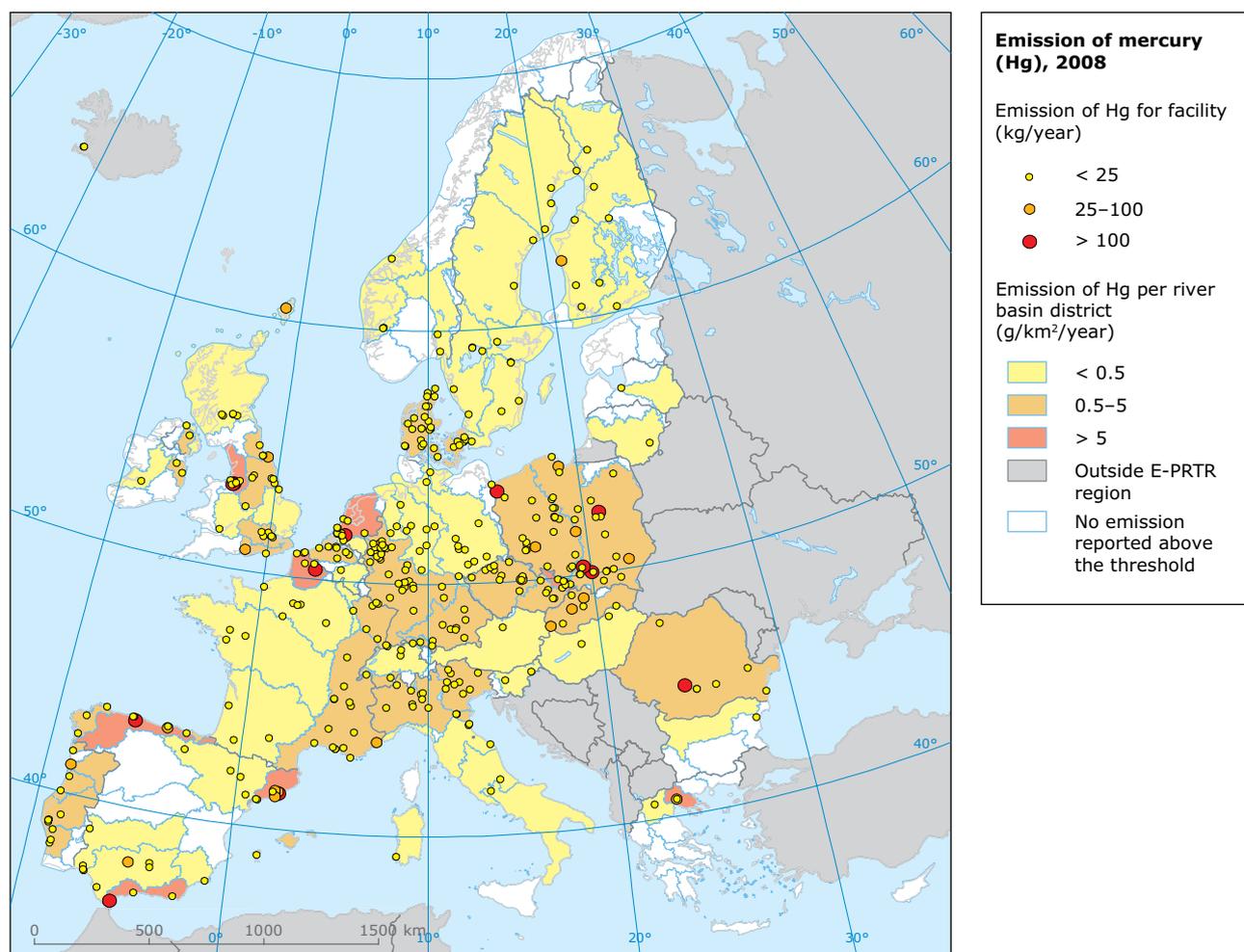
Note: Reported emissions (releases) relate to the following E-PRTR sectors: animal and vegetable products from the food and beverage sector; chemical industry; energy; mineral industry; paper and wood production and processing; production and processing of metals; waste and water management; other activities.

Source: Version 2 published on 31 March 2010 (http://www.eea.europa.eu/data-and-maps/data/member-states-reporting-art-7-under-the-european-pollutant-release-and-transfer-register-e-prtr-regulation-3).

1) Facilities smaller than the E-PRTR thresholds (and not, therefore, required to report under the regulation) including many urban wastewater treatment plants, may contribute significant emissions of mercury to water.

2) Diffuse sources, which are also not reported under E-PRTR, may be of significance.

3) Reporting under E-PRTR for mercury may well be incomplete.

The EU's mercury strategy is a comprehensive plan addressing mercury pollution both in the EU and globally. It has resulted in restrictions on the sale of measuring devices containing mercury, a ban on exports of mercury from the EU and rules on safe storage of mercury decommissioned by industry. The strategy contains 20 measures to reduce mercury emissions, cut supply and demand and avoid human exposure, especially to methyl mercury found in fish. A range of regulations and directives related to the strategy also plays a key role, addressing the use of mercury, emissions to air, and waste disposal.

Industry initiatives, in part driven by the IPPC Directive, are also important. For example, mercury cells are gradually being replaced by diaphragm and membrane cells in the chloro-alkali industry. As a result, mercury emissions from this industrial sector have fallen from 2.59 to 0.93 g per tonne of chlorine capacity between 1995 and 2009. Members of Euro Chlor — the association of chloro-alkali process plant operators in Europe — have voluntarily agreed to phase out the remaining use of mercury technology by the end of 2020 (Euro Chlor, 2010).

The United Nations Environment Programme (UNEP) has initiated a drive for a globally binding instrument to control and reduce mercury emissions (UNEP, 2008) and such reductions have been shown to yield large economic and societal benefits (Sundseth et al., 2010).

2.8.2 Cadmium

Due to its environmental toxicity and threat to human health, cadmium, a metal, is classified as a PHS under the EQSD, which therefore requires that all discharges, emissions and losses cease over time.

Map 2.3   Total (dry and wet) deposition of cadmium across Europe in 2008 (g/km²/year)
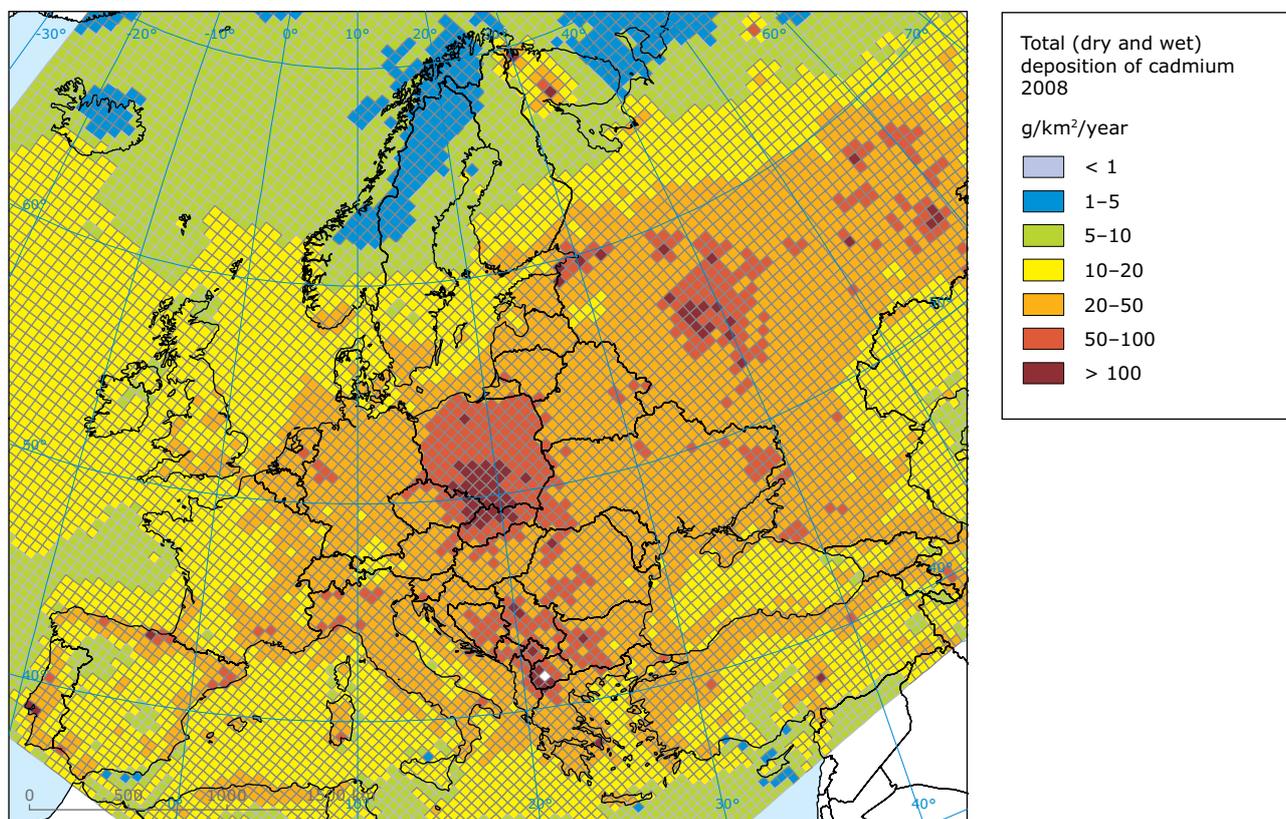
Source: European Monitoring and Evaluation Programme (EMEP).

Cadmium is primarily produced as a by-product from the extraction, smelting and refining of zinc and other non-ferrous metals. It has predominantly been used in rechargeable nickel-cadmium batteries, although sales to consumers have now been banned in Europe, with the exception of certain uses. Cadmium is also used in the production of pigments, coatings and platings.

Emissions of cadmium to air arise primarily from combustion processes in power plants and industry. Emissions to water arise from the chemicals and metals industries, the transport sector and waste streams, although other sectors, including agriculture, can also be involved. Agricultural sources of cadmium derive from the phosphate rock used to manufacture fertiliser. It is also found in animal feeds

and hence in cattle fodder and manure. Whilst metals are generally well retained in soil, studies in the Netherlands indicate that about 25 % of the cadmium load to Dutch surface waters derives from agriculture (RIVM, 2008a).

Cadmium emissions to air are ultimately deposited onto land or directly into fresh and marine waters. Atmospheric deposition in urban areas will typically result in cadmium being washed from impervious surfaces, collected and discharged to a receiving water, either directly or via a wastewater treatment plant. Combined wet and dry deposition of cadmium across Europe is variable, generally ranging between 10 and 50 g/km^2/year but reaching in excess of 100 g/km^2/year in parts of central and south-eastern Europe (Map 2.3). Across the 32 EEA

Map 2.4   Emissions of cadmium to water based on E-PRTR reporting of 2008 data
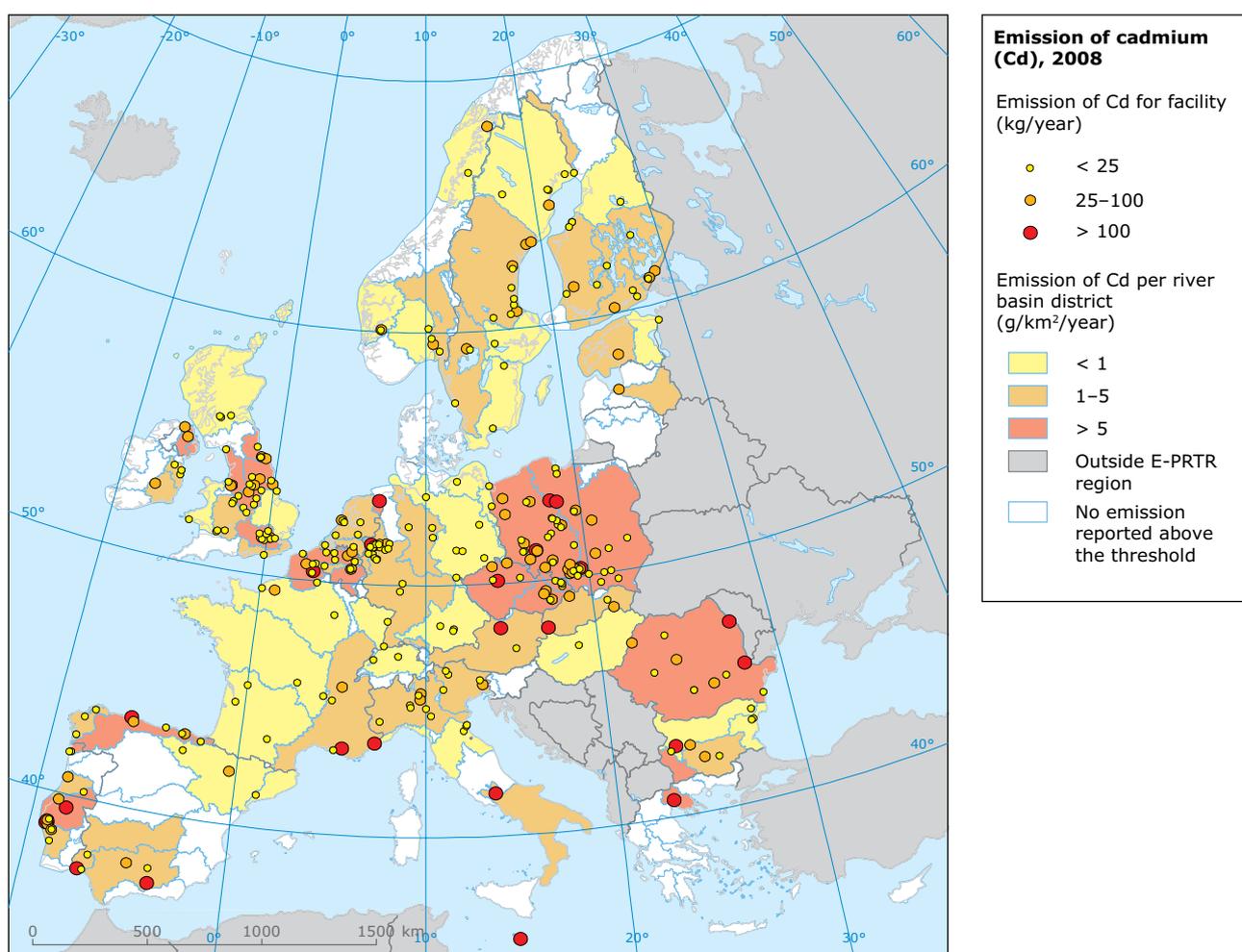
Note: Reported emissions (releases) relate to the following E-PRTR sectors: animal and vegetable products from the food and beverage sector; chemical industry; energy; mineral industry; paper and wood production and processing; production and processing of metals; waste and water management; other activities.

Source: Version 2 published on 31 March 2010 (http://www.eea.europa.eu/data-and-maps/data/member-states-reporting-art-7-under-the-european-pollutant-release-and-transfer-register-e-prtr-regulation-3).

member countries, emissions of cadmium to air have declined significantly over recent years — by about 58 % between 1990 and 2008. This decline reflects improvements in abatement technologies at industrial facilities and, in some countries, the closure of older plants as a result of economic restructuring.

Cadmium in industrial wastewater will, typically, be directed to a treatment plant, either on site or at a municipal facility. In the latter case, it is frequently combined, prior to treatment, with cadmium washed from urban land. A proportion of the metal in the wastewater will then be discharged to a receiving water within treated effluent. Typically, however, the relative contribution of the various original sources of cadmium emitted to municipal wastewater treatment plants is not well quantified. Map 2.4 illustrates cadmium emissions to water across Europe, arising predominantly from industrial facilities and urban wastewater treatment plants, as reported under E-PRTR. In 2008, 333 facilities and plants across Europe reported a total combined cadmium emission to water of 21.6 tonnes. As with mercury, however, the E-PRTR data for cadmium cannot be viewed as reflecting total emissions to water, as smaller facilities and diffuse sources are not taken into account, and the reporting may be incomplete. Emissions of cadmium to air, as reported under E-PRTR, totalled about 19 tonnes in 2008.

2.8.3 *Benzo[a]pyrene*

Benzo[a]pyrene (B[a]P) is a PAH classified as a PHS under the EQSD. Achieving the required cessation in emissions to water will be challenging, however, given that it reaches surface waters primarily through atmospheric deposition and, like other PAHs, can be found in remote areas away from human activity. B[a]P results from incomplete combustion processes, such as those related to the production of electricity, the transport sector, various industrial sectors and waste incineration.

Substance flow analysis (SFA) undertaken within the 'Source control options for reducing emissions of priority pollutants' (ScorePP) project has produced estimates of B[a]P emissions in a semi-hypothetical case city (SHCC) typical for the eastern part of Europe, with a population of 1.2 million (see Chapter 5 for a description of the approach). The results confirm the dominance of the release to air (Figure 2.1) with the potential for significant indirect emissions to surface water following subsequent atmospheric deposition. Emission reduction measures with respect to B[a]P primarily need to focus upon combustion processes, including those related to the transport sector as well as coal- and wood-powered heating and electricity-generating plants.

Figure 2.1   **Estimated emissions (kg/year) of B[a]P, broken down by compartment within a semi-hypothetical case city**
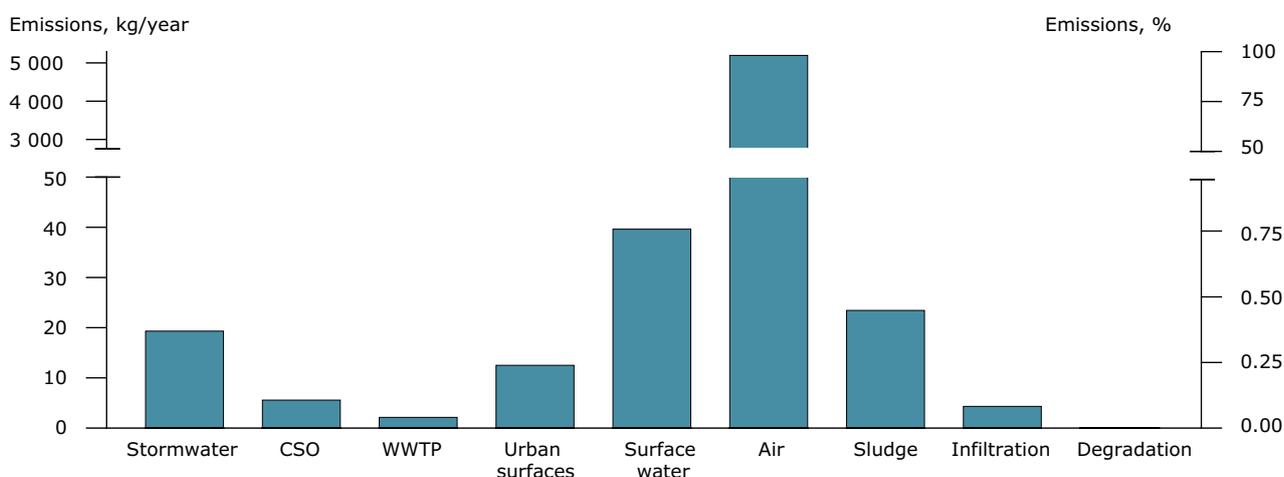
Note: 'Surface water' corresponds to the sum of emissions within the 'Stormwater', 'CSO', 'WWTP' and 'Urban surfaces' compartments. 'Air' reflects emissions directly to air. 'Sludge' represents B[a]P within sludge generated by the wastewater treatment plant (WWTP) and CSO treatment. The 'Infiltration' compartment refers to stormwater sediment and infiltration to groundwater.

Source: ScorePP.

2.8.4 Human and veterinary medicines (pharmaceuticals)

The occurrence and impacts of pharmaceutical products in the environment is an emerging concern that encompasses a range of human and veterinary medicines, including antibiotics, anti-depressives, anti-epileptics, anti-inflammatories, beta-blockers and parasiticides. Whilst production and consumption data are limited across Europe, in Germany alone, more than 9 000 pharmaceuticals with 3 000 different active compounds are registered for human use, with an annual consumption of approximately 31 000 tonnes (BPI et al., 2006).

The release of human medicines to freshwater occurs through various routes. After administration, they are absorbed, metabolised and then excreted to a sewer system — often only slightly transformed or even unchanged. In addition, despite take-back schemes, unused medicines are often disposed of improperly via the sink or toilet. Typically incomplete removal techniques at urban wastewater treatment plants (Heberer, 2002; Miège et al., 2009; Reemtsma et al., 2006) mean that drug residues or their transformation products are found in treated effluent discharged to receiving waters (e.g. Ashton et al., 2004; Gros et al., 2010) and, as a consequence, in the receiving waters themselves. Human medicines have also been detected in groundwater, including drinking water sources, where bank filtration or artificial groundwater recharge has occurred downstream from municipal sewage treatment works (Heberer, 2002). The presence of pharmaceuticals in groundwater can also derive from other sources, such as sewer leakage (Ellis, 2006) and landfill leachates (as a result of disposal via domestic waste) (Ahel and Jelicic, 2001).

Following use in livestock treatment, veterinary drugs and any metabolites may be released to soil directly, by animals at pasture, or indirectly, through the application of animal manures and slurries to land as a fertiliser (Boxall et al., 2003 and 2004). Veterinary medicines that are released to soil may subsequently be transported to surface waters via run-off or field drains (Burkhard et al., 2005; Kay et al., 2005) or leach to groundwaters (Blackwell et al., 2007). Another important route of input of livestock medicines to water bodies is wash-off from impervious farmyard surfaces. In aquaculture treatments, the drug is often added directly to the aquatic environment. Limited amounts of compounds may also be released to the environment from the treatment of companion animals or the improper disposal of unused products (Boxall et al., 2004). The potential for a veterinary medicine to be released to the aquatic environment depends on various aspects, such as the method of treatment, agriculture or aquaculture practices, environmental conditions and the properties of the medicine (Metcalfe et al., 2008).

2.8.5 DEHP

Di(2-ethylhexyl)phthalate (DEHP) is an organic compound classified as a PS under the WFD, as a substance of very high concern under REACH and as a reprotoxic (category 1B) substance under Regulation (EC) 1272/2008 on the classification, labelling and packaging of substances and mixtures. DEHP is used as a plasticiser in polymer products (mainly in flexible PVC) including pipes and tubes, flooring and wall lining, sealants, food packaging, cables and wire sheathing, underseal for cars, guttering, tarpaulins, clothing and footwear, toys, office supplies and medical products such as blood bags and catheters. The content of DEHP in polymer products varies but typically approximates 30 %, although it migrates slowly from such products over their lifetime.

A proportion of the DEHP released to the aquatic environment stems from discharge of effluent from municipal sewage treatment plants, deriving originally from the wide use of PVC in residential, commercial, medical and industrial premises and their direct connection to a sewer system. DEHP is also released into urban run-off. In this case, it originates from building materials and vehicles and is subsequently discharged to a water body directly or indirectly, via a municipal treatment plant. Stormwater overflows are also a significant emission pathway (OSPAR, 2006).

DEHP has low water solubility, and leaching from plastics in landfills is, therefore, relatively slow. Its low volatility means that emissions of DEHP to air from PVC materials are low, although loss to air does occur during waste incineration. Data reported to E-PRTR (Map 2.5) show that 17.9 tonnes of DEHP were emitted to water from 180 facilities in 2008, 97 % of which was emitted via 143 urban wastewater treatment plants. However, given its widespread use and the high likelihood of DEHP discharges from all large municipal wastewater treatment plants, Map 2.5 suggests that reporting under E-PRTR is incomplete. Estimates from other sources indicate that diffuse emissions — not reported under E-PRTR — are also a significant source of DEHP (OSPAR, 2006).

Map 2.5 Emissions of DEHP to water based on E-PRTR reporting of 2008 data
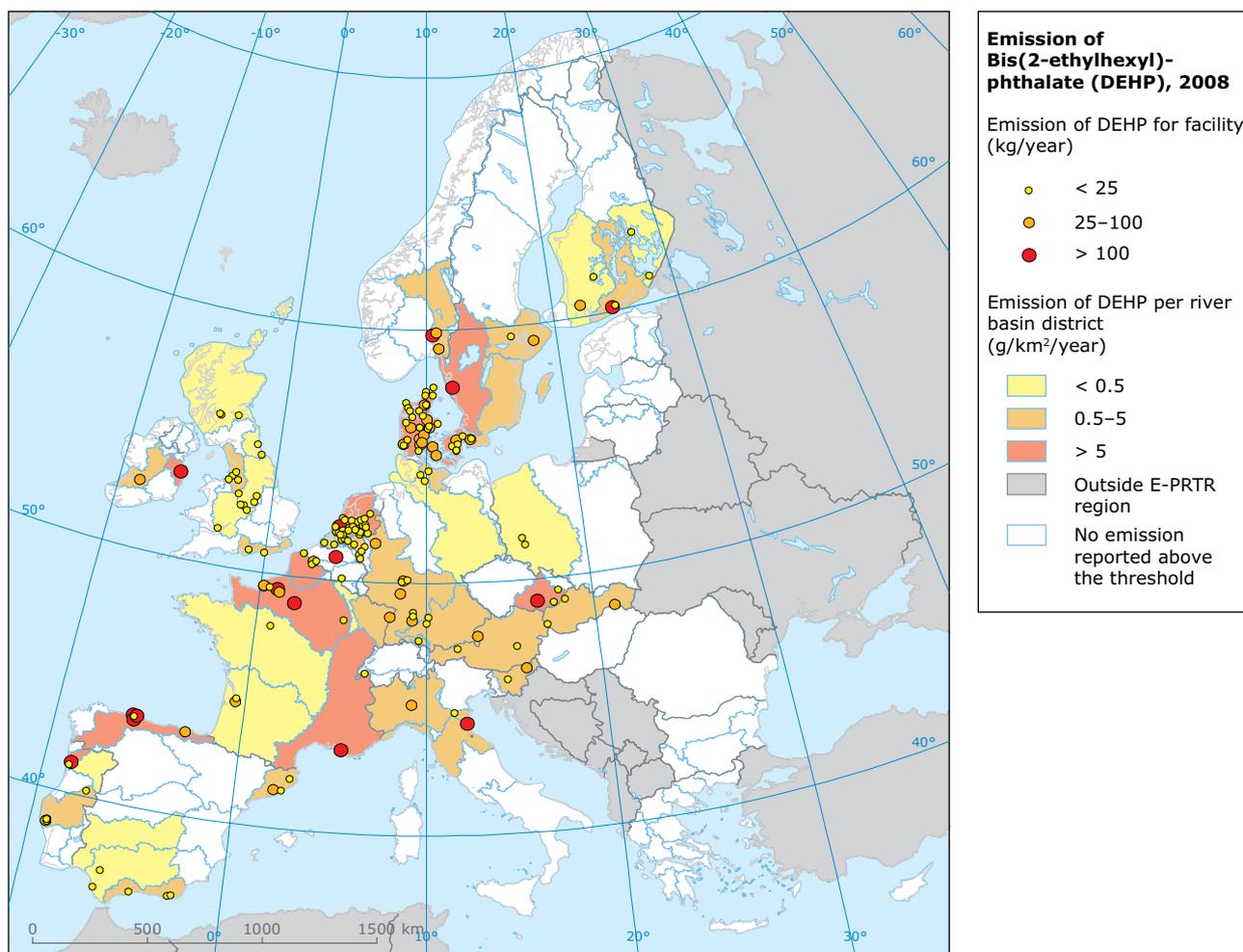
Note: Reported emissions (releases) relate to the following E-PRTR sectors: animal and vegetable products from the food and beverage sector; chemical industry; energy; mineral industry; paper and wood production and processing; production and processing of metals; waste and water management; other activities.

Source: Version 2 published on 31 March 2010 (http://www.eea.europa.eu/data-and-maps/data/member-states-reporting-art-7-under-the-european-pollutant-release-and-transfer-register-e-prtr-regulation-3).

2.8.6 Endocrine-disrupting chemicals

Concerns have existed for a number of years about the potential for a heterogeneous group of substances in the environment to interfere with the normal functioning of endocrine systems, affecting reproduction and development in both humans and wildlife. Such endocrine-disrupting chemicals (EDCs) have been defined as 'exogenous substances that alter function(s) of the endocrine system and consequently cause adverse health effects in an intact organism, or its progeny, or (sub)populations' (WHO/IPCS, 2002).

A large range of naturally occurring and man-made substances have been shown to have potentially endocrine-disrupting properties. These include pesticides, fungicides, insecticides, industrial chemicals like PCBs, PAHs, alkylphenols, phthalates and dioxins, chemicals in personal care products (e.g. triclosan, an antimicrobial in hand soaps), and synthetic oestrogens in pharmaceutical products such as oral contraceptives and hormone replacement therapy drugs.

Discharges of municipal and industrial wastewater are a major route of EDCs entering the aquatic environment. Treatment can remove much of the influent load (e.g. Andersen et al., 2003; Baronti et al., 2000; Johnson and Williams, 2004), resulting in low concentrations (typically parts per trillion) being discharged within effluent to receiving waters. However, such low concentrations, especially of highly biologically active steroid hormones, can

still result in endocrine disruption in aquatic biota (Jobling et al., 2006).

The occurrence of endocrine disruption in freshwater fish in areas not directly affected by discharges from sewage treatment plants indicates that other sources exist (Bjerregaard et al., 2008). Livestock, for example, are also a source of oestrogenic hormones, and studies in surface waters draining intensive livestock farms suggest that levels may be high enough to cause endocrine disruption in some aquatic organisms (e.g. Matthiessen et al., 2006; Orlando et al., 2004). In Denmark, steroid hormones from pig manure have been observed to leach through soil, rapidly reaching subsurface tile drains at significantly high concentrations, a process exacerbated by macropore flow (Kjær et al., 2007). The typically high connectivity of such agricultural tile drains

to surface waters raises the risk of contamination of rural streams by EDCs. Endocrine-disrupting activity has also been documented for certain pesticides in current use.

Rural housing is often unconnected to municipal sewage treatment plants and simple wastewater processing measures such as septic tanks may be employed. Septic tanks are relatively ineffective at removing oestrogens from wastewater, and oestrogenic activities 20 times higher than levels needed to feminise brown trout have been detected in discharges from such systems (Stuer-Lauridsen et al., 2005). Leguminous plants — such as clover, peas, lupins and alfalfa used as nitrogen-binding crops for example in organic farming — produce phyto-oestrogens which may leach to and are detected in the freshwater environment (Bjerregaard et al., 2011; Ribeiro et al., 2009).

3 Hazardous substances in water, aquatic biota and sediment — current concentrations and recent trends

3.1 Introduction

This chapter summarises information from a variety of sources that document the presence of a range of hazardous substances in Europe's fresh and marine waters as well as associated biota and sediment. It describes current concentrations and, where possible, compares these against existing legislative criteria. Some recent trends are also identified. The information is based on data drawn from a variety of sources, including chemical status as reported under the RBMPs of the WFD; the EEA's Eionet-Water database, which holds freshwater and marine data reported by EEA member countries; monitoring programmes conducted by the JRC; regional sea

conventions (HELCOM and OSPAR) and European research studies. However, despite the improved knowledge base arising from this body of information, very often uncertainty remains as to whether the observed concentrations of a particular substance pose a risk to aquatic environments and human health.

3.2 Chemical status of Europe's water bodies as reported under the WFD

3.2.1 Surface waters

Under the WFD, Member States were required to report chemical status for fresh and coastal water

Map 3.1   WFD chemical status of surface water as of December 2010
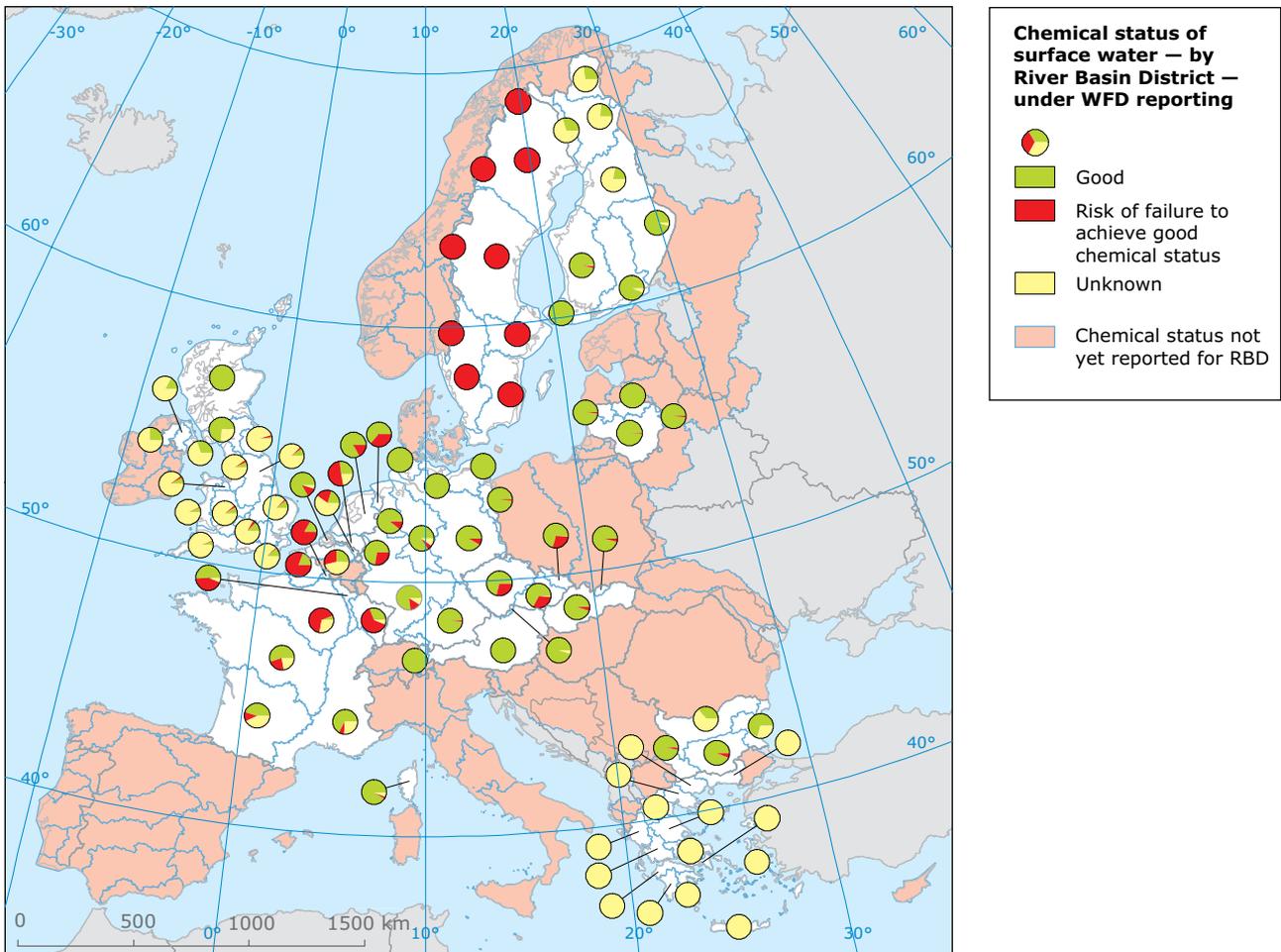
Source: EEA based on information reported by Member States in the RBMPs.

bodies in 2010 (as part of the RBMPs). Map 3.1 summarises this information for surface waters at river basin district (RBD) scale and describes the relative proportion of water bodies of good status, those at risk of failing to achieve good status and those of unknown status. The map reflects information as reported by December 2010. It should be noted that assessment of these plans is ongoing, and that the conclusions advanced below remain tentative. Additionally, it is beyond the scope of this report to present all the background information supplied in each of the plans. Consequently, only certain issues have been highlighted.

Excessive levels of metals including cadmium and mercury challenge good chemical status in a number of RBDs to have reported by December 2010, including those in the Czech Republic, Germany and the United Kingdom. In Sweden, widespread excessive levels of mercury in aquatic biota mean that all RBDs currently fail to achieve good chemical status. Very few other priority substances in Sweden are of concern, however, other than locally. In Sweden, biota has been chosen as the matrix for monitoring, making detection more likely than in the water column, given the propensity of mercury to bioaccumulate. In at least one other Member

State, however, a water column (i.e. less stringent) EQS is known to have been used with respect to mercury. Such inconsistency in reporting between Member States is of concern.

PAHs are identified as being problematic, including in the Elbe and Rhine international river basins, raising the challenge of how to meet the EQS given that these substances are primarily released to and deposited from the atmosphere and can be transported over long distances. TBT levels in some UK coastal and estuarine waters threaten good status whilst a proportion of UK freshwater bodies are at risk from diffuse pollution by agricultural pesticides. The Joint Danube Survey 2 was undertaken in 2007 to provide an overview of status throughout the Danube river system. Whilst the results do not replace national assessments, they do provide an indication of chemical status and have identified DEHP, PAHs, nonylphenol, TBT and trichlorobenzene as being of concern; 44 % of water samples exceeded the EQS for DEHP.

3.2.2 Groundwater

Good groundwater chemical status is based upon compliance with EU-wide standards for pesticides and nitrates and threshold values established by

Figure 3.1   Number of GWBs at poor chemical status due to cadmium, lead and mercury
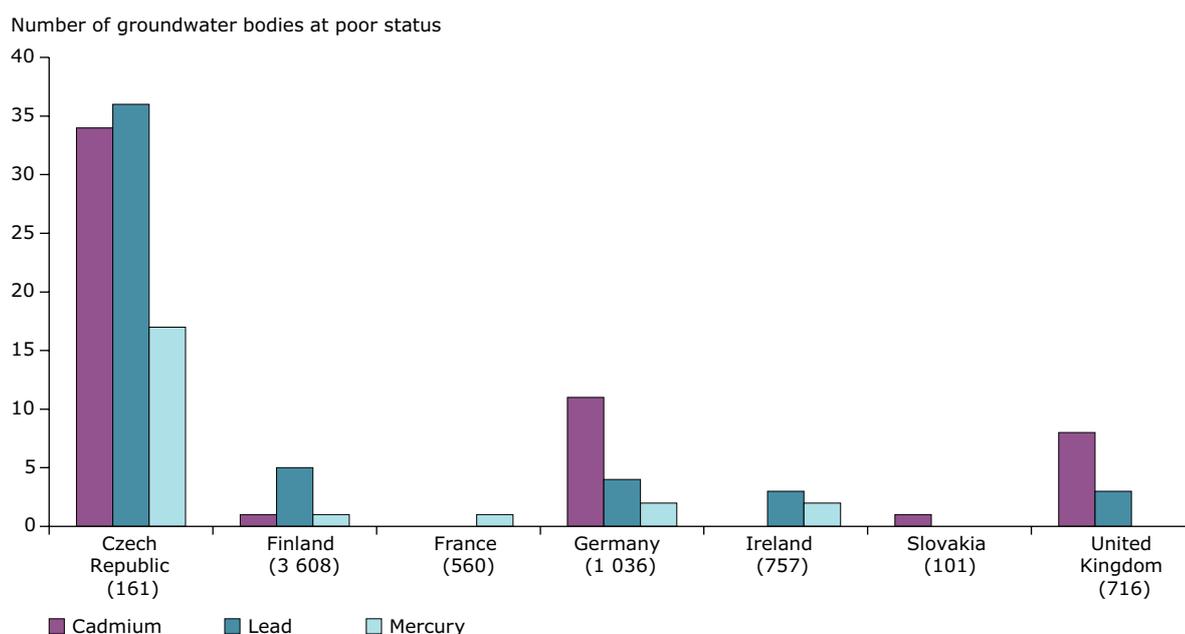
Number of groundwater bodies at poor status

Note: The figures in parentheses indicate the total number of GWBs in each country. The established thresholds vary between Member States. No groundwater bodies (GWBs) at poor status due to any of these three heavy metals exist in Belgium, Bulgaria, Estonia, Latvia, Lithuania, Hungary, Malta, Netherlands, Austria, Poland, Romania, Slovenia and Sweden. No information was reported for any of these three heavy metals in Denmark, Greece, Spain, Cyprus, Italy and Luxembourg.

Source: EC, 2010a.

Figure 3.2   Number of GWBs at poor chemical status due to arsenic and tri- and/or tetrachloroethylene

Number of GWBs at poor chemical status
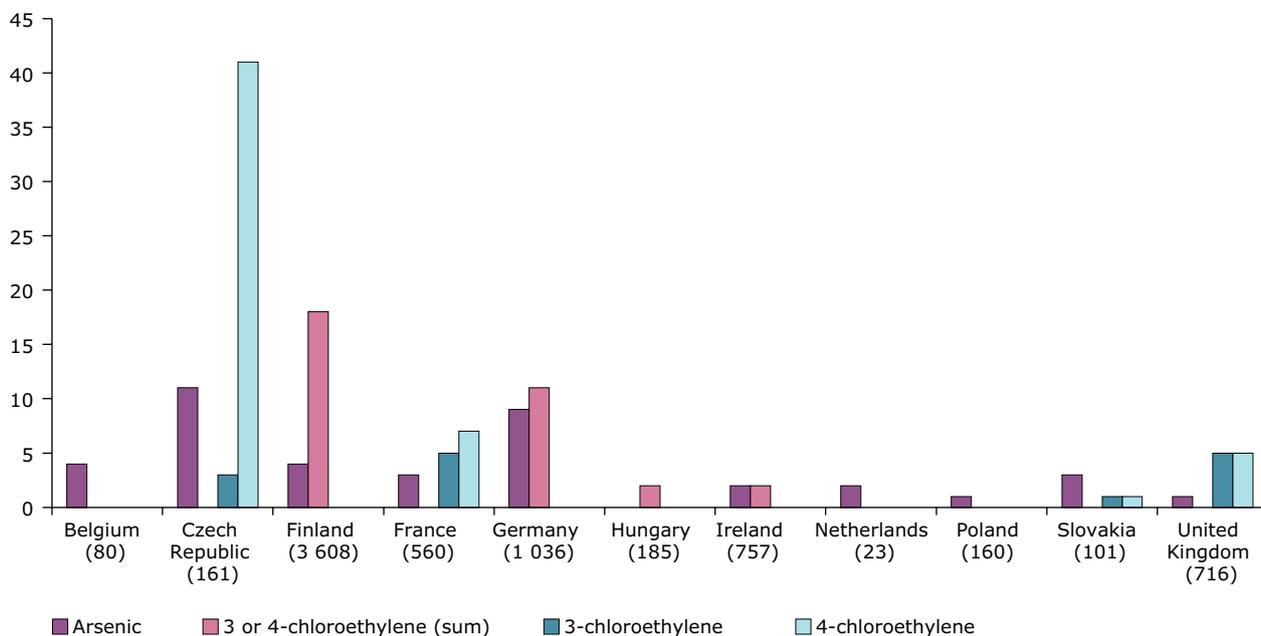
Note: The figures in parentheses indicate the total number of GWBs in each country. The established thresholds vary between Member States.
For arsenic: no GWBs at poor status exist in Bulgaria, Estonia, Latvia, Lithuania, Hungary, Malta, Austria, Portugal, Romania and Slovenia. No information was reported for Denmark, Greece, Spain, Cyprus, Luxemburg and Sweden. Italy has reported GWBs at poor status but has not specified a number.
For tri- and tetrachloroethylene: no GWBs at poor status exist in Belgium, Bulgaria, Estonia, Latvia, Lithuania, Malta, Netherlands, Austria, Portugal, Romania and Slovenia. No information was reported for Denmark, Greece, Spain, Cyprus, Luxemburg, Poland and Sweden. Italy has reported GWBs at poor status but has not specified a number.

Source: EC, 2010a.

the Member States for other pollutants, as defined under the Groundwater Directive. Recent reporting by Member States of those substances that give rise to poor chemical groundwater status illustrates that contamination by heavy metals occurs in some Member States (Figure 3.1) whilst levels of arsenic (Figure 3.2) and tri- and tetra-chloroethylene (Figure 3.2) are also observed to sometimes exceed the established thresholds. However, these thresholds often vary considerably between Member States. Full details of this reported information are provided in EC, 2010a. Pesticides too are observed to exceed the thresholds, although declining trends are evident, for example, in German groundwater (UBA, 2010).

3.3   Pan-European monitoring of organic substances

The JRC has recently organised a large-scale sampling and monitoring programme at 122 river stations and 164 groundwater sites in 27 European countries in order to obtain a pan-European

perspective on the occurrence and levels of a range of organic substances, including many of those considered to be emerging pollutants (Loos et al., 2009 and 2010). Emerging pollutants are those for whom the potential for adverse effects has only recently become apparent (in contrast, for example, to metals and organochlorines) and for which the understanding of sources, emissions, levels and effects in the aquatic environment remains limited.

Across the JRC study, nearly 60 organic substances were investigated. These include pesticides, pharmaceuticals, hormones, antibiotics, perfluorinated surfactants and other industrial chemicals. In total, more than 100 collaborators joined the monitoring campaigns and samples were analysed in 5 expert laboratories. The information gathered is of value in determining whether a particular substance is of pan-European relevance or if it is a local issue. In addition, technical guidance and best practice for analysing priority substances has arisen from the work to support implementation of the WFD (Lepom et al., 2009; Loos et al., 2009).

However, for several of the monitored substances, threshold concentrations or environmental quality standards for freshwater have yet to be set.

3.3.1 Rivers

The average frequency of detection for all compounds in rivers was 61 %, with the highest median concentrations being found for nonylphenoxyacetic acid (a degradation product of surfactants, 233 ng/l), benzotriazole (an aromatic compound commonly used as a corrosion inhibitor, 226 ng/l), and carbamazepine (a pharmaceutical, 75 ng/l). In addition, relatively high average concentrations (> 50 ng/l) were found for ibuprofen (a pharmaceutical), nonylphenol (an alkylphenol used as a surfactant), sulfamethoxazole (an antibiotic) and isoproturon (a herbicide), whilst

the highest maximum concentrations (> 500 ng/l) were measured for isoproturon, diuron (a herbicide), nonylphenol and tert-octylphenol (a surfactant) — all of which are classified as PSs under the EQSD. Pesticides were generally found at relatively low concentrations, potentially because the survey was conducted in autumn. The results for atrazine broadly support those reported to the EEA.

3.3.2 Groundwater

For the groundwater monitoring exercise (Loos et al., 2010), the list of substances selected for monitoring in rivers was supplemented by additional compounds, primarily pesticides. The average frequency of detection for all compounds in groundwater was 25 %, with the most frequently detected including caffeine, perfluorooctanoic

Figure 3.3   Frequency of detection for selected substances (% of samples) in rivers and groundwater
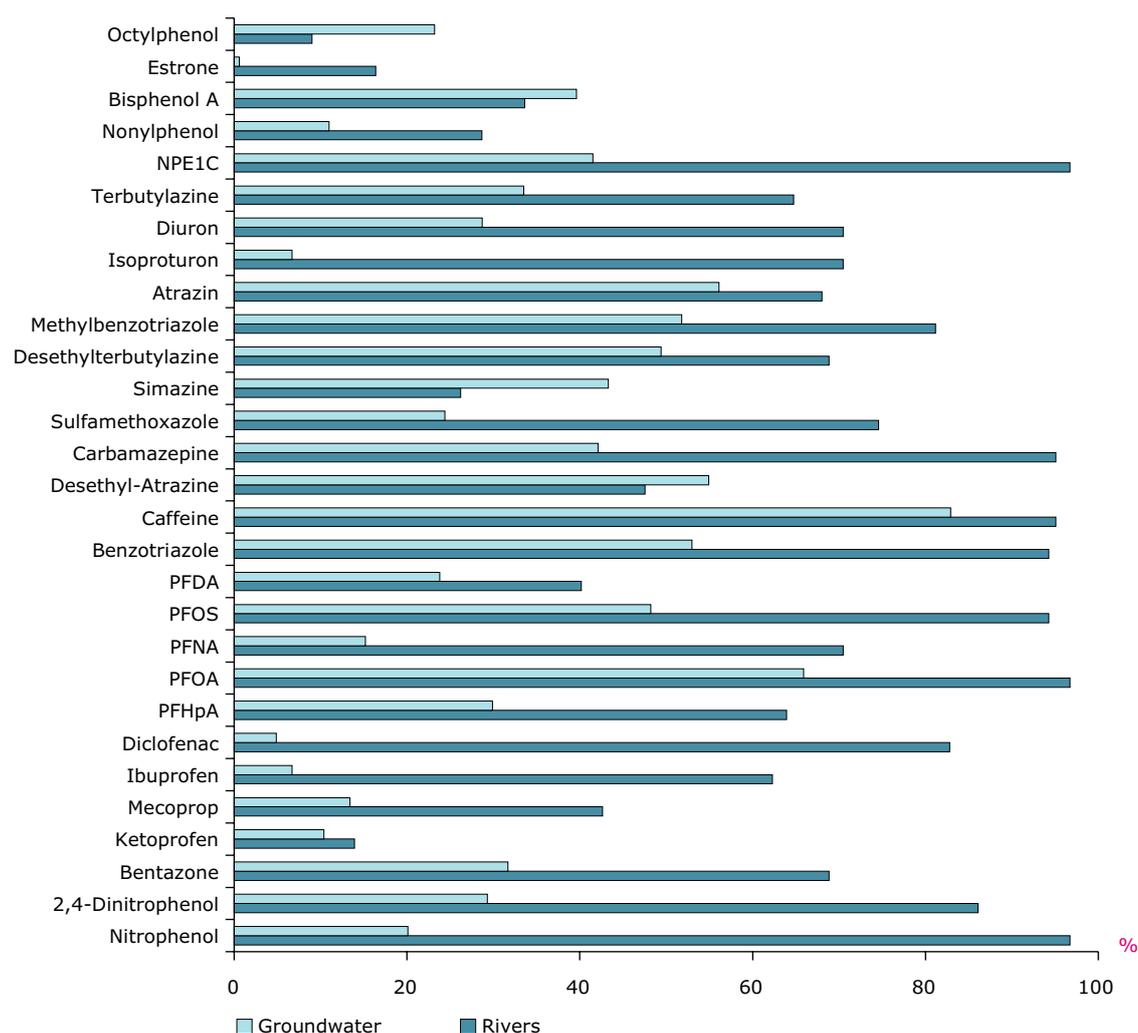
Source: Loos et al., 2009; Loos et al., 2010.

Box 3.1   The triazine pesticide group

Triazine pesticides are of particular concern with regard to freshwater contamination due to a number of their properties, including a relatively high water solubility, persistence (long half-life) and low soil adsorption. Of the triazine pesticides, both atrazine and simazine have been used as herbicides (by inhibition of photosynthesis) on cropland, on transport highways and domestically. Both, however, have now been banned and are classified as PSs under the EQSD.

Despite the ban, data reported under Eionet indicate that both pesticides remain evident in groundwaters across Europe. Map 3.2, for example, illustrates which substances in the triazine group of pesticides have been found in groundwater in recent years, on at least one occasion, at concentrations greater than 0.1 µg/l. This is the standard established under both the Groundwater Directive and the Drinking Water Directive. In addition to atrazine and simazine, both the transformation products of atrazine — desethylatrazine and desisopropylatrazine — and terbuthylazine, an active substance replacing atrazine, have also been found at concentrations exceeding the standard (Map 3.2). It should be noted, however, that the frequency of exceedance for the triazine pesticides is relatively low for all countries reporting to the EEA. In addition, gradual declines in the frequency of detection of triazine pesticides have been reported over recent years.

Data reported to Eionet describing concentrations of atrazine and simazine in European rivers indicates that, for all 16 countries providing data, no exceedance of the EQS is observed. This is likely to reflect the ban and its relatively quick impact upon river concentrations relative to those in groundwater. In French rivers, for example, detection of atrazine has fallen from more than 60 % of analyses in 2002 to about 15 % in 2007.

Map 3.2   Triazine pesticides in groundwater between 2003 and 2008
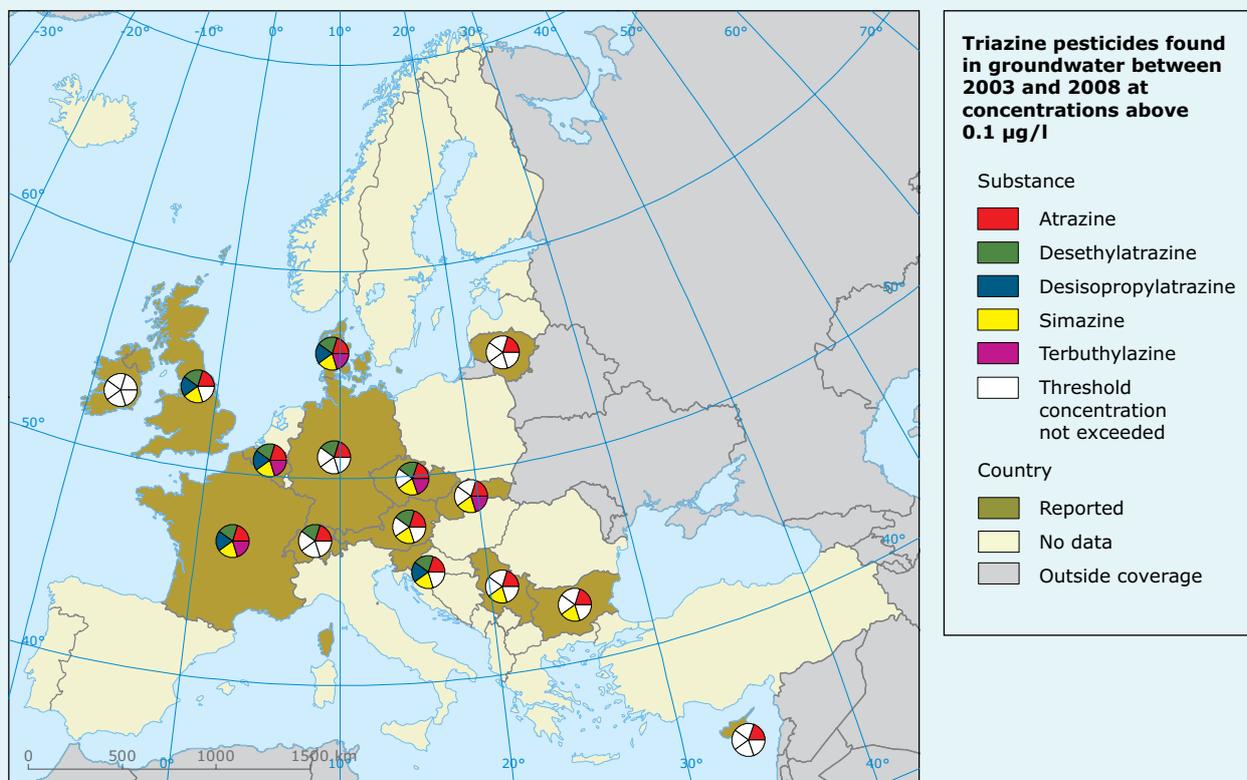
Note: The pie charts indicate the occurrence, on at least one occasion, of concentrations above the limit of 0.1 µg/l. The data shown do not reflect the frequency with which the threshold has been exceeded.

Source: Data were sourced from Eionet and, in the case of Denmark, supplemented by information from the Danish national groundwater monitoring programme (1989–2007) and the Geological Survey of Denmark and Greenland.

acid (PFOA, a fluorosurfactant), atrazine and desethylatrazine (DEA, a metabolite of atrazine). Overall, substances were detected less frequently in groundwater than in rivers (Figure 3.3), although some exceptions to this observation were apparent, notably for simazine (a herbicide), bisphenol A (an organic compound used to make plastics) and octylphenol. However, those substances found with high frequency did not necessarily have the highest concentrations. Across the survey, 29 % of all groundwater samples contained at least one pesticide exceeding the EU limit of 0.1 μg/l for groundwater and drinking water, for a single pesticide. In 10 % of samples, the EU limit of 0.5 μg/l for total pesticides was exceeded.

In addition to the JRC monitoring programme, a number of recent European research studies have contributed to a growing, although still incomplete, understanding of the levels of various hazardous substances in water, including some of those viewed as emerging pollutants. These studies include surveys of pharmaceuticals in freshwater in Spain (Ginebreda et al., 2010) and the United Kingdom (Ashton et al., 2004) and heavy metals in the Seine (Meybeck et al., 2007). A recent survey of PAH levels in the sediment of high mountain lakes in Europe showed total concentrations in all lakes to be above the no-effects threshold (Quiroz et al., 2010). This finding highlights the challenge of addressing substances that are largely ubiquitous, subject to transport over large distances in the atmosphere and detectable in remote regions away from human activity.

Veterinary medicines have received little attention with respect to their monitoring within aquatic environments. One exception is a UK study (Boxall et al., 2006) involving the continuous monitoring of water and sediment at farms where veterinary medicines were known to be in use, in order to determine typical exposure profiles in rural streams. Maximum concentrations of antibacterials in stream water ranged from 0.02 (trimethoprim) to 21.1 (lincomycin) μg/l, whilst the parasiticides (doramectin and ivermectin) were not detected. Concentrations of antibacterials in sediment were 0.5–813 μg/kg and those of doramectin and ivermectin were 2.7 and 4.9 μg/kg respectively.

3.4 Transitional, coastal and marine waters

Riverine loads and direct discharges of hazardous substances to coastal waters are not, as a rule, widely reported across Europe, although the OSPAR regions of the North Atlantic form an exception. Here data are available for five hazardous substances, which include three metals (cadmium, mercury and lead), the insecticide lindane and PCBs, a group of chemicals previously widely used in electrical equipment.

Despite some uncertainties in the data and the need for caution in interpretation, downward trends are detected for all five substances as regards their total inputs to the OSPAR region (Figure 3.4; OSPAR, 2009e). For example, statistically significant downward trends in combined riverine inputs and direct discharges of mercury to the Greater North Sea and Celtic Sea regions, of about 75 % and 85 % respectively, are reported for the period 1990–2006. The decline observed for the Greater North Sea is supported by data from the Rivers Elbe, Meuse and Rhine, all of which illustrate decreases of 65–70 % in riverine inputs of mercury over this period. Significant downward trends for cadmium are also apparent; these are attributed to declines in both riverine inputs and direct discharges. Reductions to the Greater North Sea region reflect, in part, a 40 % decline in riverine inputs from the River Elbe (OSPAR, 2009e). Downward trends in lead are also observed, with substantial decreases apparent in the Rivers Rhine and Seine. In addition to the decline in metal emissions to air (see earlier case studies), these trends observed in the OSPAR regions are also attributed to a decline in emissions to water, both through the implementation of best available abatement techniques at industrial facilities and improvements in municipal wastewater treatment (OSPAR, 2009e). Aside from the metals, marked declines in lindane and PCBs are clearly apparent (Figure 3.4), reflecting a ban on the use of both.

Despite the high number of hazardous substances with the potential to contaminate the marine environment, information with sufficient geographical and temporal coverage to enable a pan-European assessment is limited. A collation of data from HELCOM, OSPAR and the EEA member countries has, however, enabled an assessment of the levels of seven hazardous substances in marine biota — in the North-East Atlantic, the Mediterranean Sea and the Baltic Sea. The substances include the five previously described with respect to inputs to OSPAR waters, plus a further insecticide (dichlorodiphenyltrichloroethane (DDT)) and a fungicide (hexachlorobenzene (HCB)). This assessment complements the information provided within the RBMPs of the WFD with respect to transitional and coastal waters. It does not, however, reflect official national assessment of chemical status.

Figure 3.4   Input of hazardous substances (via riverine loads and direct discharges) into the North-East Atlantic during the period 1990 to 2008

Source: OSPAR.

Maximum levels in fish, molluscs and crustaceans have been set for the three metals in order to protect public health (Regulation (EC) 1881/2006). These maximum levels are used in this analysis (Map 3.3) to establish the threshold boundary between moderate and high concentration. For the other contaminants discussed here, alternative approaches to establishing such thresholds have been used, including OSPAR's background assessment concentration (BAC) and ecotoxicological assessment criteria (EACs). Trend information encompasses the period 1998 to 2008.

All seven substances can be found at high concentrations in all three of these European seas. In the case of DDT, HCB, lindane and PCBs, this observation reflects their persistence in the aquatic environment, given that all four are now banned within Europe. In certain locations, metal concentrations exceed the maximum levels set by legislation. In the Mediterranean Sea, lindane concentrations exhibit a declining trend, although some sites show an upward trend in mercury and lead. In the North-East Atlantic, concentrations of cadmium, DDT, lead, lindane and PCBs are all

declining, reflecting the decrease in riverine loads. Declining trends are also evident for lindane in the Baltic Sea, although data from other sources (not shown) indicate declining trends in PCBs in herring, perch and mussels in several locations in the Baltic Sea (HELCOM, 2010).

In the Black Sea (data not featured in Map 3.3), concentrations of lindane and DDT in sediment have been found to be five times higher than the Russian standards for extremely high pollution (EEA, 2010a). Metal pollution represents a particular problem in the Danube estuarine region and large ports, although in some areas concentrations appear to be decreasing (Korshenko et al., 2008). Petroleum hydrocarbon pollution in Romanian and Turkish waters exceeds threshold values by a factor of 16 (EEA, 2010a).

3.4.1   Other hazardous substances in the marine environment

Whilst Europe-wide data are not available, the banning of TBT has led to clear downward trends of concentrations in marine snails in the OSPAR

Map 3.3   Assessment of hazardous substances in biota in the North-East Atlantic Sea, Baltic Sea and Mediterranean Sea

Aggregated assessment of hazardous substances measured in the North East Atlantic Sea including the North Sea, Baltic Sea and Mediterranean Sea

- Low concentrations
- Medium concentrations
- High concentrations
- North East Atlantic Sea
- Baltic Sea
- Mediterranean Sea
- Black Sea

Cd:	Cadmium
Hg:	Mercury
Pb:	Lead
HCB:	Hexachlorobenzene
Lindane:	Gamma hexachlorocyclohexane (Y - HCH)
DDT:	Dichlorodiphenyltrichloroethane
PCB:	Polychlorinated biphenyls

Trend up   Trend down

Source: EEA, 2011.

region (OSPAR, 2009a). A similar outcome is evident in the HELCOM region, with clear declines in TBT levels in mussels, eelpout and whelks (HELCOM, 2010). In both sea regions, however, high levels of TBT in sediment are still found locally, reflecting the historical use and persistence of this substance. Although European legislation restricts the use of perfluoroalkyl substances (used as surfactants), they are widely found in marine birds and mammals in the Baltic (HELCOM, 2010). Limited information is available with respect to emerging pollutants in the European marine environment and, to date, no Europe-wide monitoring programme — equivalent to the one undertaken by the JRC for freshwater — has been launched. However, a growing number of research studies indicate a potential cause for concern notably for pharmaceuticals and personal care products (Näslund et al., 2008; Roberts and Thomas, 2006; Xie et al., 2008).

3.4.2   The Arctic

Hazardous substances, including persistent organic pollutants (POPs) and mercury, are present in parts of the Arctic where there are no human activities to explain the contamination. This observation shows that the region acts as a sink for pollutants that have been transported over long distances, by rivers, air and ocean currents. Some of these substances accumulate in marine foodwebs and therefore in

humans, and their concentrations in both can reach much higher levels than in water and air.

International policy efforts have, however, produced positive effects on the levels of some substances. The Stockholm Convention on POPs and the Aarhus Protocol on POPs, for example, have led to a decline in POPs in Arctic air and wildlife, although concentrations are still high enough to affect the health of top predators, such as polar bears, in the marine food web (AMAP, 2009). Perfluorinated compounds are detected in Arctic marine life, with an initial increased trend occurring from the initiation of data collection in the mid-1980s. A less consistent picture has been apparent in recent years. Some declining levels of perfluorooctanesulfonic acid (PFOS) have been noted in sea otters from Alaska and ringed seals and beluga whales from the Canadian Arctic.

These trends are consistent with the decline in the production of PFOS; however, there are current sources that may continue to contribute inputs to the environment (AMAP, 2009). Brominated flame retardants are also detected in Arctic marine life, with increasing trends broadly following the production and use up to the early 2000s. There is some evidence, however, that concentrations are starting to level off or decline, at least in some areas (AMAP, 2009), in line with restrictions upon the use of these substances in recent years. Clear declines in riverine load and direct discharges of lead and cadmium to Arctic waters are reported, although insufficient data are available with respect to mercury (OSPAR, 2009e).

4 Impacts of hazardous substances in water

4.1 Introduction

This chapter addresses the impacts of hazardous substances on the health of aquatic ecosystems and the potential for risks to human health. It reviews documented detrimental impacts on both freshwater and marine life and highlights a few substances of concern. The risks to human health from hazardous substances in the wider environment are briefly addressed. However, in line with the central themes of this report, more detailed analysis is restricted to the potential for human exposure via water, namely the chemical contamination of food from aquatic sources and the contamination of drinking water. Excessive levels of chemicals in water also give rise to economic impacts, such as the significant capital and operating costs associated with water and wastewater treatment.

4.2 Impacts on aquatic ecosystems

Numerous studies have documented a range of detrimental impacts of hazardous substances upon aquatic ecosystems, particularly in freshwater, estuarine and coastal environments, but also in the open sea. Observations from aquatic ecosystems in the 1950s and 1960s were the first 'early warnings' of the environmental dangers of the widespread production and use of industrial and man-made chemicals. The effects, for example, of methyl mercury, organochlorines and pesticides such as DDT on seabirds and marine mammals are well documented (Hario et al., 2004; Helander et al., 2009; Sørmo et al., 2005).

The early studies identified chemical properties which were particularly important with respect to environmental effects and which later became important criteria for classification and labelling in chemical legislation. Examples of these are lipid solubility (lipophilicity, hydrophobicity), persistence, and bioaccumulation potential. The mechanism of biomagnification became apparent: chemicals are enriched higher up in the food chain, resulting in the highest levels in top predators like tuna or salmon, fish-eating birds, marine mammals (seals, dolphins) and eventually humans. With increased knowledge, concern with respect to new groups of substances has grown, and whilst these are often only present in the aquatic environment

at very low concentrations, such levels can still be sufficient to cause detrimental impacts.

Here, the overview of impacts upon aquatic ecosystems focuses on documented effects linked to four groups of substances: pesticides, human and veterinary medicines, personal care products and nanomaterials, with the latter three groups falling into the category of emerging pollutants. In addition to these aspects, the overview includes an initial focus upon a particular category of effect in aquatic biota — the phenomenon of endocrine disruption. It should be noted that oestrogenic effects can be caused by a range of chemicals including pesticides and pharmaceutical products. Combination effects arising from the presence of several chemicals are also significant.

4.2.1 Endocrine disruption

The egg yolk protein vitellogenin is used as a biomarker (i.e. a change in a biological response at molecular, cellular or physiological level that can be related to exposure to or toxic effects of environmental chemicals) for oestrogenic effects. Increased levels of vitellogenin in the blood of female or male juvenile fish that are not sexually mature mean that they have been exposed to substances with oestrogenic activity. Another sign of endocrine disruption, also related to oestrogen exposure, is intersex characterised by the presence of eggs in the testes of male fish (Jobling et al., 2006; Nolan et al., 2001).

Numerous studies across Europe document the occurrence of sexual disruption of freshwater fish found in the proximity of effluent discharges from wastewater treatment plants. Jobling et al. (2006), for example, report that intersex in roach in the UK was significantly correlated with predicted concentrations of oestrogens in river reaches receiving treated sewage effluents. In the Netherlands, elevated concentrations of vitellogenin were observed together with an increased prevalence of intersex in wild male bream in a small river receiving treated sewage (Vethaak et al., 2005). Both *in situ* and laboratory bioassays showed oestrogenic hormones to be primarily responsible for these effects. In Spain, vitellogenin was found to be increased in male carp downstream of a sewage treatment plant (Petrovic et al., 2002) whilst in Italy,

50 % of barbel sampled below a polluted tributary of the River Po showed intersex gonads (Viganò et al., 2001). Endocrine disruption of male fish has also been recorded in the Czech Republic, both in a polluted stretch of the River Elbe downstream of three major chemical plants (Randak et al., 2009) and downstream of the city of Brno (Blahová et al., 2010). Additionally, laboratory studies have shown that the combined effects of EDCs can be additive, whereby such chemicals at levels, individually, below which any effects can be detected, result in observable detrimental effects when combined (Brian et al., 2005). EDCs have been observed to cause effects in other freshwater biota, including mudsnails exposed via sediments (Duft et al., 2003), and identified as a potential factor in the global decline in amphibians (Hayes et al., 2002).

Endocrine disruption in estuarine and marine environments has also been documented. Elevated blood vitellogenin concentrations were observed in male dab (Scott et al., 2007) and cod (Scott et al., 2006) caught in open waters of the North Sea. In both studies, the fish were far out to sea away from any direct sources of pollution. Larger fish were found more likely to have elevated vitellogenin levels, suggesting a gradual accumulation, via feeding, of oestrogenic compounds in the marine food chain. Endocrine disruption has also been detected in tuna and swordfish in the Mediterranean (Fossi et al., 2002), with the latter being linked to PCB concentrations in the fish (Fossi et al., 2004). In the United Kingdom, investigative programmes in several estuaries have found endocrine disruption in flounder, a bottom-dwelling flatfish particularly exposed to any contamination of sediment (Thomas et al., 2004). The UK research showed that male flounder caught in industrialised estuaries, receiving effluent from sewage treatment works and industry, had elevated concentrations of vitellogenin, with cases of intersex and testicular abnormalities also recorded (Allen et al., 1999). Also of note, however, is evidence of a lessening in the degree of endocrine disruption over time in some UK estuaries, a finding in line with improvements to the treatment of wastewater (Kirby et al., 2004; Kleinkauf et al., 2004). Improvements have also been noted elsewhere, with a declining trend in imposex being observed, for example, in whelks netted in Danish coastal waters of the Belt Sea (Strand, 2007).

In some cases oestrogenic effects are known to be irreversible (Rodgers-Gray et al., 2001), and in severely feminised fish, fertility is reduced, raising implications for population survival (Jobling et al., 2002). An illuminating example is the experiment by Kidd et al. (2007), where a synthetic oestrogen

was introduced to a whole lake in the Canadian Experimental Lake Area for seven years, at concentrations found in polluted environments (5–6 ng/l). Male fathead minnows showed clear signs of feminisation (vitellogenin and intersex), while altered egg development was observed in females. Strikingly, within seven years, fathead minnows were almost extinct from the lake, clearly illustrating that endocrine disrupters can threaten the sustainability of wild fish populations.

4.2.2 Pesticides

Pesticides are rigorously risk assessed before being approved for marketing. However, their use, particularly if it does not follow relevant guidance, can lead to harmful effects upon non-target organisms in the wider environment, including freshwater biota. Aside from the potential for oestrogenic effects (Tyler et al., 2000), severe impairment of the nervous system of several fish species has been observed in Lake Balaton, Hungary, following the use of deltamethrin, a synthetic pesticide used for the extermination of mosquitoes on the shores of the lake (Csillik et al., 2000).

Insecticide run-off has also been shown to adversely affect freshwater macroinvertebrates in agricultural streams. Schulz and Liess (1999), for example, found that short-term contamination during rainfall events led to acute effects including the loss of 8 of the 11 common macroinvertebrate species normally present in a stream, with a significant reduction in population density of the remaining 3 species. Beketov et al. (2008) also found that short-term exposure to pesticides causes long-term changes to invertebrate communities, whilst a toxicity-related shift from sensitive to more tolerant or opportunistic species was observed for aquatic biota exposed to pesticides in agricultural field drains (De Zwart, 2005).

Despite these and other studies, knowledge of the ecotoxicological effects of pesticides upon aquatic biota remains limited. In particular, very little is known about the impact of products formed by transformation of the parent pesticide compound or about the risk of additive or synergistic effects that may arise from the use of agricultural pesticides in combination with one another.

4.2.3 Human and veterinary medicines

Human medicines
Whilst concentrations of human medicines in Europe's water bodies are not likely to be high

enough to cause acute toxicity to freshwater biota, chronic exposure to low concentrations may potentially give rise to sublethal effects (De Lange et al., 2006). Hoeger et al. (2005), for example, showed that the presence of the anti-inflammatory drug diclofenac, at concentrations comparable to those found in freshwater, caused adverse effects in the kidneys and gills of trout. Similarly, Triebskorn et al. (2007) observed effects in the gills, liver and kidneys of trout and carp exposed to four different pharmaceuticals, again at environmentally relevant concentrations.

Documented adverse effects are not limited to freshwater fish. De Lange et al. (2006), for example, found a significant decrease in the activity of *G. pulex*, a freshwater benthic invertebrate, when exposed to the antidepressant fluoxetine and the analgesic ibuprofen. Concern also exists with regard to the potential for antibiotics and steroid drugs to cause resistance among natural bacterial populations (Obst et al., 2006).

Impacts of pharmaceuticals upon marine organisms have also been observed. The osmoregulatory ability of the green shore crab *Carcinus maenas* was impaired when exposed to diclofenac (Eades and Waring, 2010), whilst the antiepileptic drug carbamazepine gave rise to detrimental effects upon Mediterranean mussels (*Mytilus galloprovincialis*) (Martin-Diaz et al., 2009). In addition, clotrimazole, used for the treatment of fungal infections, has been shown to impact upon single-celled algae, the basis of the oceanic food chain (Porsbring et al., 2009).

Veterinary medicines
Information on the effects of veterinary medicines on aquatic organisms (fish, invertebrates and algae) needs to be generated as part of the marketing authorisation process for veterinary medicinal products in Europe. Comparison of maximum measured concentrations with predicted no-effect concentrations for a range of veterinary medicines indicates that, typically, these substances probably do not pose a great risk to the aquatic environment. Exceptions, however, are apparent. These include antibiotics that are particularly toxic to cyanobacteria (Halling-Sørenson, 1999) and, similarly, anti-parasitic compounds with respect to invertebrate species (Lopes et al., 2009).

The suitability of standard regulatory studies for assessing the environmental risks of veterinary medicines has, however, been questioned, with the use of other, more subtle and chronic endpoints being advocated. For example, concerns have been raised over the potential for veterinary antibiotics in the environment to select for antimicrobial resistance in bacterial communities (Boxall et al., 2003).

4.2.4 Personal care products

Personal care products (often grouped with pharmaceuticals with respect to their environmental pathways and impact) include cosmetics, fragrances, lotions, shampoos, soaps, toothpastes and sunscreens. They are primarily released to water via wastewater discharges (Muñoz et al., 2008) although direct release of sunscreens via bathing also occurs.

As in the case of other emerging substances, understanding of the effects of personal care products in aquatic ecosystems remains incomplete, although some toxicological studies indicate a potential concern. UV filters used in sunscreens and cosmetics, for example, have been shown to cause oestrogenic effects in fish, both individually (Christen et al., 2011) and in mixtures (Kunz and Fent, 2006). They are also linked to the bleaching of corals (Danovaro et al., 2008).

4.2.5 Nanomaterials

Nanotechnology has great potential for industry and society, with a wide range of varied applications that include electronics, optics, textiles, medical devices, cosmetics, food packaging, fuel cells, catalysts, biosensors and environmental remediation including water treatment technology (Handy et al., 2008). Nanotechnology is expanding rapidly, and further research is needed to better understand the associated risks and to ensure the protection of human health and the environment (EC, 2009a). Release of nanomaterials to the environment occurs via production sites, landfills, waste incineration plants and wastewater treatment facilities, with the latter including nanoparticles in both treated effluent and sewage sludge (Gottschalk et al., 2009; Limbach et al., 2008).

Little information is available on the environmental toxicity of nanomaterials, although a growing number of laboratory studies are adding to the knowledge base. Such research includes the impact of manufactured nanomaterials upon aquatic biota, notably for water fleas (Oberdorster et al., 2006), fish (Smith et al., 2007) and molluscs (Tedesco et al., 2010). Once released to the environment, nanoparticles have the potential to interact with and alter the bioavailability of hazardous substances. The bioaccumulation of cadmium in fish, for example, was found to be enhanced in the

Box 4.1 Chemical mixtures in the aquatic environment

Monitoring surveys of European freshwaters show that aquatic organisms are often exposed to a mixture of hazardous substances in their natural environment. Under current chemical legislation, however, hazardous substances are tested and risk assessed as single entities and not in the mixture in which they occur in the environment. As a consequence, the actual risks to aquatic environments could well be underestimated (Kortenkamp et al., 2009).

There are several possible mechanisms by which substances can potentially interact. They can, for example, add to each other's toxicity or augment each other's toxicity. It is also possible for one substance to block the toxicity of another. One of the best-established blocking mechanisms is that of chelating chemicals, like ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DPTA), which reduce the toxicity of metals like copper or zinc by binding them in strong complexes which are not bioavailable. EDTA, DPTA and similar substances are added to detergents as so-called 'water softeners', since they also bind calcium.

There is currently intense scientific activity to develop and refine models facilitating predictive assessments of the environmental hazards associated with such mixtures. So-called component-based approaches (CBAs) are based on the ecotoxicological characterisation of individual mixture components and a subsequent linking to the toxicity of the resulting mixture. Such studies often aim to develop a fundamental understanding of how chemical mixtures behave in relation to the toxicity, modes and mechanisms of action of their components, the exposure conditions as well as the physiology and ecology of the exposed organisms. One goal is to develop mixture assessment tools that can be used in predictive risk assessments, in particular for developing EQSs for chemical mixtures. Another important aim of CBAs is to provide a rationale on how to identify toxicologically important compounds in complex environmental samples. CBA studies typically use the concept of concentration addition (CA) and (to a lesser extent) independent action (IA) to predict the expected mixture toxicity implicitly or explicitly.

Compared to the available data for freshwater and terrestrial systems, the empirical evidence with respect to the joint action of chemicals in the marine environment is limited. Therefore, it is unclear whether the special chemistry of natural marine waters in combination with the type of pollutants typically found in the marine environment has an impact on the predictive power of either concept. One pattern, however, seems to be common amongst the vast majority of ecotoxicological mixture studies: the joint mixture toxicity is clearly higher than the toxic effect of each individual compound at the concentration present in the mixture. This has important implications for the definition of EQSs for aquatic environments, as it clearly indicates that setting an EQS for an individual substance is a necessary first step, but that compliance with that standard does not *a priori* safeguard against mixture effects.

presence of titanium dioxide (TiO_2) nanoparticles (Zhang et al., 2007), whilst the sorption of a PAH to nano carbon tube aggregates increased toxicity to algae and daphnids (Baun et al., 2008). Such interactions must, therefore, be accounted for in risk assessments and are a parallel to the issue of chemical mixtures.

4.3   Human health and chemicals in the environment

Human exposure to certain chemicals in the environment has been associated with declining sperm counts, genital malformation, impaired neural development and sexual function, obesity and cancer (EEA, 2010b). Of particular concern

are persistent and bio-accumulative substances, endocrine-disrupting chemicals and heavy metals. Periods of embryonic, foetal and infant development are known to be particularly sensitive to chemicals, and toxic exposure at these times can cause disease and disability across the span of human life (Gee, 2008; Grandjean et al., 2007). Evidence is growing that early-life or prenatal exposures are linked to some adult-onset diseases, and some effects may even be trans-generational (EEA, 2007). However, assessing the impacts of chemicals on human health is highly complex and uncertain, due to differences in individual vulnerability, the time lag between critical exposure and (mostly non-specific) health outcomes, the role of other modifying factors (such as nutrition or social conditions), and exposure conditions (typically long-term, low-level exposure

to a mixture of chemicals) (EEA, 2007 and 2010b; Gee, 2008).

Evidence for human exposure to a range of hazardous substances is strong and derives, in particular, from studies using biomarkers, i.e. measures of chemicals or their metabolites within a biological matrix. For example, samples of blood (including that from the placenta), urine, breast milk, and hair show that numerous chemicals are found in the human body (Calafat et al., 2009; CDC, 2009; Edginton and Ritter, 2008; Vieth et al., 2005). These studies have contributed to the growing recognition that risk assessment needs to account for the potential synergistic effects of human exposure to a mixture of chemicals. Cumulative risk assessment is necessary to avoid a likely underestimation of risks under the current paradigm of considering substances on a chemical-by-chemical basis (EEA, 2010b). Concern with respect to 'chemical cocktails' is reflected in recent European Council conclusions (Council of the European Union, 2009).

Human exposure to toxic chemicals can occur, in broad terms, via inhalation, ingestion and direct contact with skin. The latter can arise from the use of personal care products and household chemicals but also via inappropriate handling of industrial chemicals. Exposure via inhalation is dependent upon ambient air quality, although indoor air including household dust plays a role. In addition, exposure to spray drift of chemicals, including pesticides, can be of importance locally (RCEP, 2005). Ingestion via terrestrially grown food can pose a risk where chemicals have been applied to agricultural land. The European Food Safety Authority (EFSA) reports on pesticide residues in food commodities in the EU, Iceland and Norway. In 2008, more than 70 000 samples of nearly 200 different types of food were analysed for pesticide residues by national authorities, with 96.5 % of the samples complying with the legal maximum residue levels (MRLs) of pesticides (EFSA, 2008). Human exposure to veterinary drugs can also occur via crops; antibiotics in pig manure applied to cropland have been found to be incorporated, via the roots, within winter wheat (Grote et al., 2007). Hazardous substances found within treated biosolids arising from municipal wastewater treatment can also potentially raise concerns for human health where those biosolids are subsequently applied to agricultural land (Clarke and Smith, 2011). However, European limits have been set for the levels of metals in sludge intended for agricultural use. Certain chemicals can also contaminate foodstuffs via their migration from packaging.

Chemical contamination of food from seafood and freshwater fish also presents a risk, although this needs to be balanced against the health benefits of consumption (Gochfeld and Burger, 2005; Sioen et al., 2008). Further risk is associated with untreated or inadequately treated drinking water, and the potential for exposure via these two water-related pathways is explored in more detail in the following section. Despite some research (e.g. Fromme et al., 2009) understanding of the relative risk posed by each of the exposure routes outlined above remains largely incomplete, with a general lack of quantitative information.

4.4 Human exposure to hazardous substances via water

4.4.1 Contaminated seafood and freshwater fish

Persistent hazardous substances found in aquatic environments can bio-accumulate throughout the food chain, raising implications for human health with respect to the consumption of seafood (fish, crustaceans, molluscs and marine mammals) and freshwater fish. The bio-accumulation of mercury and various POPs in particular can cause health concerns for vulnerable population groups (EC, 2004; EFSA, 2005). Dietary mercury, for example, is almost completely absorbed into the blood and distributed to all tissues including the brain. It also readily passes through the placenta to the foetus and foetal brain (Sundseth et al., 2010), with women of childbearing age being regarded as the population group of greatest concern (Mergler et al., 2007).

The Arctic provides a prominent example of the exposure of humans to hazardous substances through the consumption of food from the marine environment. Monitoring of contaminant levels in the Arctic population over the past decade indicates that human exposure to POPs and metals is declining, reflecting reduced environmental contamination, dietary changes (most dietary energy now comes from store-bought supplies rather than from traditional food sources in the Arctic (AMAP, 2009)) and health advice to vulnerable population groups. Human biomonitoring data for PCBs, mercury and lead indicates that the percentage of women whose test results exceed health guidelines is declining over time. However, despite the declines, more than 75 % of women sampled in Greenland exceed the US evaluation levels for mercury of 5.8 mg per litre of blood. In addition, over a third exceeds the Canadian increased risk range threshold of 20 mg/l (AMAP, 2009).

A number of European studies examining the potential for exposure to hazardous chemicals via seafood have been undertaken, with the results varying with region, population group and the substance of concern. In the Baltic Sea, for example, organochlorine levels in salmon and herring were found to exceed EU maximum permissible levels (Isosaari et al., 2006), with Finnish consumption levels of herring likely to exceed recommended intake limits for these substances (Kiljunen et al., 2007). The EU limits for mercury are exceeded in blue mussels of Horsens Fjord, Denmark (HELCOM, 2010). In Flanders, exposure of recreational fishermen to PCBs through eel consumption is of concern, with the Belgian PCB standard for fish being exceeded in 80 % of sampled localities (Bilau et al., 2007). In Italy, levels of dioxin-like PCBs were found to be twice as high in farmed sea bass as in those caught wild, a finding attributable to contaminated feed with respect to the former (Carubelli et al., 2007). In a Norwegian study, seafood was found to be a major source of perfluorinated compounds in humans; however, tolerable daily intakes were not exceeded (Haug et al., 2010). In Catalonia, average exposure of children to a range of contaminants through fish and seafood consumption was found not to exceed tolerable daily intake (Martí-Cid et al., 2007), whilst organochlorine compounds in seafood from the Spanish Atlantic south-west coast were also below EU regulatory levels (Bordajandi et al., 2006).

4.4.2 Contaminated drinking water

The Drinking Water Directive (and comparable non-EU legislation) sets quality standards for water at the tap, based on guidelines issued by the World Health Organization (WHO), for a range of microbiological and chemical parameters. Much of Europe is now connected to municipal systems supplying treated water under quality-controlled conditions. However, reporting under the Directive (for the period 2002–2004) indicates some non-compliance with respect to a range of chemical parameters including iron, manganese, aluminium, arsenic, trihalomethanes, lead, nickel, PAHs and chloride. In addition, individual pesticides cause non-compliance but were often covered by derogations during this reporting period (EC, 2007).

In recent years, concern has been raised with respect to the presence of some emerging pollutants within treated municipal drinking water. In the United States, for example, pharmaceuticals and endocrine disrupter compounds have been found in drinking water distribution systems (Benotti et al., 2009) whilst the presence of pharmaceuticals in drinking water in Europe has also been documented (Sadezky et al., 2008). Pharmaceuticals have also been detected in bottled mineral water (Perret et al., 2006). Understanding of the effects of long-term human exposure to trace amounts of such substances — in concentrations of parts per billion or trillion — remains incomplete.

In some, typically rural, areas of Europe, the local population relies upon small individual or community-managed non-piped supplies of water, usually wells or boreholes. Such small-scale supplies are not covered by the Drinking Water Directive and the provision of safe drinking water can present a challenge: any chemical (or microbiological) pollution of groundwater in the vicinity of such wells will pose a threat to public health. The World Health Organization reports that chemical contamination of drinking water across the (WHO) pan-European region, whilst restricted to specific local areas, can have a significant impact upon human health (WHO, 2010).

Nitrates in drinking water represent a special case. Whilst not considered a hazardous substance according to the meaning of the term in this report, excessive levels of nitrate in ground and drinking water raise health concerns, in particular for infants, young children and pregnant women. Excessive exposure to nitrates in water in infants and young children can cause deficiencies of oxygen transport in blood (methaemoglobinaemia) leading to 'blue baby' syndrome. Contamination of well water with nitrate occurs across Europe, and cases of infant methaemoglobinaemia have been reported (WHO, 2011).

5   Protecting Europe's fresh and marine waters from chemical pollution

5.1   Introduction

A range of EU, regional and national legislation has been implemented in Europe to address the use of chemicals and their emission to the environment, including fresh and marine waters. Collectively this legislation aims to reduce risks to human and ecosystem health through a variety of approaches, which include bans on production; restrictions on marketing and use; public participation and the raising of public awareness; requirements to demonstrate implementation of clean production and best available techniques in applications for industrial permits; requirements with regard to the disposal of waste; fiscal instruments; the obligation for producers and importers to prove that their chemical substances are harmless; emissions standards including the requirement to reduce or, in some cases (e.g. PHSs), cease discharges, emissions and losses of hazardous substances to water; and the establishment of EQSs for aquatic ecosystems.

A number of elements in this suite of legislation require or encourage the control of hazardous substances at source, an approach generally more cost-effective than treatment following release. The possibilities for source control are varied and often specific to particular pollutants. Examples include the implementation of legislative limits for the amount of zinc in tyres and construction materials, and the use of available alternatives to replace copper in brake linings, roofs and water pipes (RIVM, 2008b).

Photo: © Hans-Christian Holten Lützhøft, (DTU Environment)

Box 5.1 Reducing emissions of priority substances in the urban environment

The 'Source control options for reducing the emissions of priority substances' (ScorePP) project has explored the effectiveness of emission control strategies (ECSs) at reducing emissions of priority substances within the urban environment. The approach involves the development of semi-hypothetical case cities (SHCCs) which draw upon characteristics of actual cities, for example with respect to wastewater treatment, supplementing them with additional information through expert judgement. In this way, various ECSs can be explored in a consistent manner across a set of differing city types that are realistic and representative of the real world. Emissions throughout each city are estimated using substance flow analysis.

In this example, ECSs are explored within a city (population 0.5 million) broadly typical of northern Europe. The city is characterised by a consumer-orientated industry and secondary wastewater treatment, with 90 % of stormwater being collected in a combined sewer system. Six different ECSs were applied to the city. The first (ECS1) reflects a business-as-usual scenario where no additional measures (to the current situation) are taken to reduce emissions. ECS2 reflects a strategy where all relevant EU Directives are fully implemented, including the Sewage Sludge Directive, the Directives restricting certain hazardous substances in electrical and electronic equipment and the subsequent disposal and recycling of such equipment, and the Urban Waste Water Treatment Directive (although in this particular city type, full compliance has almost been achieved already under the business-as-usual scenario). In addition, best available technologies (BATs) are assumed to have been implemented where required, i.e. in larger industries. ECS3 focuses on voluntary options including educational and information campaigns, whilst ECS4 extends the BAT requirements to small enterprises. ECS5 focuses upon stormwater management practices (Scholes et al., 2008) including a reduction in the amount of impervious urban land to allow for infiltration of water and pollutants as well as enlargement of stormwater ponds to reduce CSO discharges. Finally, ECS6 addresses advanced wastewater treatment including oxidation processes and ultra-filtration.

Figure 5.1   The effects of applying various control options upon emissions of cadmium and DEHP in the urban environment
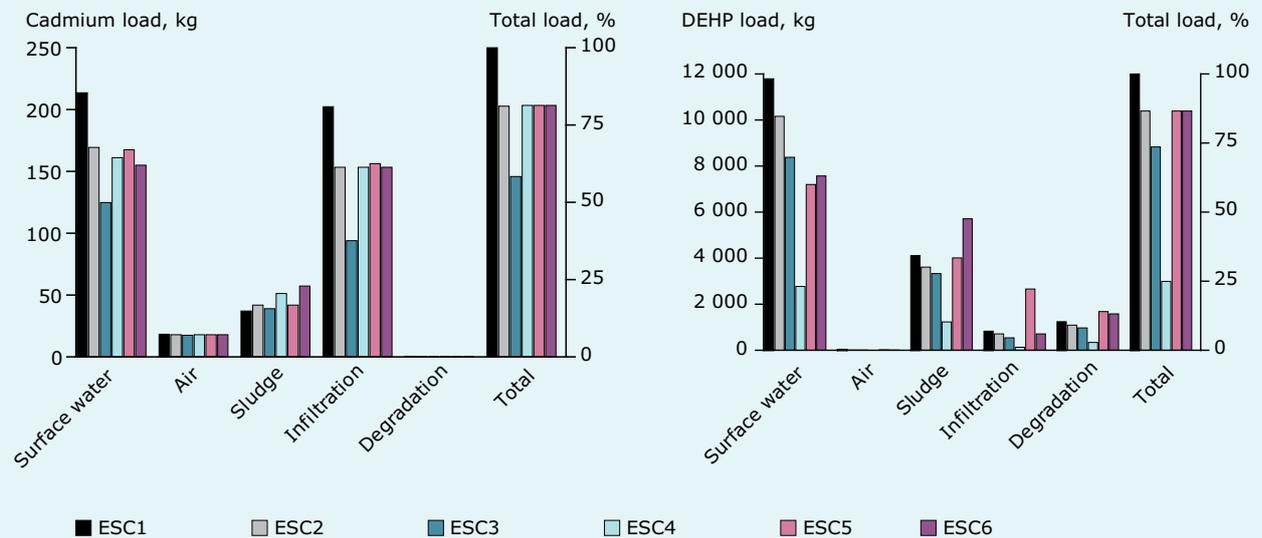
Note: See text for an explanation of each scenario (ESC). 'Surface water' also includes releases to the urban surface. 'Sludge' includes sludge from both WWTPs and CSOs. 'Infiltration' includes both stormwater sediment and infiltration to the groundwater. Changes in predicted load (kg) are provided for the various components of the urban environment (1st Y-axis), whilst the percentage change in total load is read from the 2nd Y-axis.

Source: ScorePP.

Box 5.1 Reducing emissions of priority substances in the urban environment (cont.)

The results of the ECS analysis are illustrated here (Figure 5.1) for two pollutants — cadmium and DEHP — in terms of their emissions (load) to surface water and air, their infiltration and build-up in sludge, and their degradation (which covers wastewater treatment removal processes like biodegradation and advanced oxidation processes). For both substances, a 15–20 % total reduction in emissions occurs, relative to business as usual, if EU legislation is fully implemented, whilst a further 15–20 % reduction occurs under the voluntary option strategy. A substantial decline in DEHP emitted to surface water and built up in sludge is predicted when BATs are extended to small enterprises. Both stormwater management practices and advanced wastewater treatment also lead to reduced emissions to surface water, although the latter results in increased levels of both substances in sludge. The performance of measures such as stormwater retention ponds and advanced wastewater treatment can vary with the type of hazardous substance.

Source controls for pharmaceutical products include the provision of advice on, and mechanisms for, the appropriate disposal of unused medicines and containers. Such advice could also include information on the environmental effects of inappropriate disposal. Opportunities also exist to implement green-pharmacy methods, including a reduction in the environmental impact of pharmaceutical manufacture and the creation of active ingredients which decline after use (EEA, 2010c; Kümmerer, 2007). Controls on the use of pesticides are described in section 5.5. Some source control measures are more generic and potentially applicable to a number of groups of substances. A key measure for reducing the level of purification required for Europe's drinking water, for example, is the establishment of safeguard or protection zones around the source. Such zones, recognised in the WFD legislation, need to be associated with regulatory powers to control polluting activities.

Whilst controls at source need to be fully exploited, full compliance with legislation is likely to also necessitate the implementation of various other measures to attenuate the emission of hazardous substances to water. Such measures include advanced wastewater treatment, urban stormwater controls and certain agri-environmental practices. Advanced treatment of municipal wastewater, for example, has been shown to significantly reduce the presence of endocrine-disrupting substances in treated effluent discharged to receiving waters (Andersen et al., 2003; Stuer-Lauridsen et al., 2005). In addition, advanced physical, chemical and biological methods of wastewater treatment can remove pharmaceuticals (EEA, 2010c). Revision of Swiss water protection legislation is currently being considered to specifically address greater removal of substances such as personal care products and pharmaceuticals through upgraded wastewater treatment (FOPH/FOEN, 2010).

A comprehensive review of all chemicals-related legislation in Europe is beyond the scope of this report. Instead this chapter focuses upon the key Europe-wide legislation that directly or indirectly addresses the contamination of water by hazardous substances. Whilst such water-related legislation is comprehensive, significant challenges remain, not least because some of the problems currently observed with respect to chemical contamination of Europe's aquatic environments relate to two aspects that are very difficult to address: past uses of substances that have led to accumulation within soils and aquatic sediments, and the continuous release of substances in consumer products.

5.2 REACH

EC Regulation 1907/2006 on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), managed and coordinated by the European Chemicals Agency, aims to improve the protection of human health and the environment from the risks of chemicals. REACH gives greater responsibility to industry to manage the risks from chemicals and to provide safety information on substances used. Manufacturers and importers are required to gather information on the properties of their chemical substances to allow their safe handling and to register this information in a central database. The Regulation also calls for the progressive substitution of the most dangerous chemicals once suitable alternatives have been identified. Authorisation is required for use of chemicals that cause cancer, mutations or problems with reproduction (CMR), that are persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB), or that are identified from scientific evidence as causing probably serious effects on humans or the environment.

Box 5.2 Aquatic toxicity testing

Information on aquatic toxicity is mandatory when introducing new chemicals on the market. REACH requires a 'base-set' of aquatic toxicity tests for chemicals produced or marketed at more than 10 tonnes per year. Base-set testing builds on acute toxicity tests with algae, a crustacean (*Daphnia magna*) and fish. In an acute toxicity test, organisms are exposed to different concentrations of the chemical, and the concentration killing or having a defined effect on 50 % of the organisms is established (LC-50 or EC-50). LC-50 or EC-50 is a key piece of information when making the environmental risk assessment. For chemicals below 100 tonnes per year, acute toxicity is enough, but for chemicals produced or marketed above this rate, additional tests are required to assess endpoints more subtle than death. Examples of such endpoints are reproduction, multi-generational survival, growth of juveniles and vitellogenin induction. In order to standardise the testing, the Organisation for Economic Co-operation and Development (OECD) has developed and published a number of testing guidelines.

5.3 Water Framework Directive (WFD) and Environmental Quality Standards Directive (EQSD)

The WFD, which represents the single most important piece of EU legislation relating to the quality of fresh and coastal waters, aims to attain good ecological and chemical status by 2015. The WFD includes a strong economic component and, in accordance with the polluter pays principle, requires that Member States implement cost recovery of the environmental and resource costs of water services. The implementation of cost recovery for wastewater treatment services could help to promote the control of hazardous substances at source, thereby reducing their levels in both treated effluent and biosolids at municipal plants.

The chemical status of Europe's surface waters is addressed by the EQSD, a 'daughter' directive of the WFD. The EQSD defines environmental quality standards (EQSs) in fresh and coastal waters for pollutants of EU-wide relevance known as priority substances (PSs). The EQSs associated with the PSs are defined both in terms of annual average and maximum allowable concentrations, with the former protecting against long-term chronic pollution problems and the latter against short-term acute pollution. Member States are required to monitor the PSs in surface water bodies and to report EQS exceedances. PSs designated thus far include metals, herbicides, insecticides, fungicides, biocides, volatile organic compounds, alkylphenols, PAHs and phthalates. The European Commission is required to review the list of PSs every four years and identify, where appropriate, new PSs or PHSs and any need to revise the EQSs or the status of existing PSs.

The EQSs must not only protect freshwater and marine ecosystems from possible adverse effects of hazardous substances; they must also safeguard human health, which potentially can be put at risk via drinking water or the ingestion of food originating from aquatic environments. In this way, all direct and indirect exposure routes in aquatic systems are to be accounted for when establishing the EQSs. For example, the setting of an EQS for the water column alone may be insufficient with respect to a chemical with a tendency to bioaccumulate and one which may therefore pose a risk through secondary poisoning resulting from food chain transfer. Instead, in this case, a biota standard may be required alongside the water column EQS. The technical guidance on deriving EQSs in the field of water policy has recently been revised.

In the vicinity of point discharges, concentrations of pollutants are usually higher than the ambient concentrations in water. Member States are able to make use of 'mixing zones' adjacent to the discharge point where the EQS can be exceeded so long as the compliance of the rest of the body of water with the relevant EQS is unaffected. The extent of mixing zones should be restricted to the proximity of the point of discharge and should be proportionate. Technical guidelines with respect to the identification of mixing zones have been established (EC, 2010b).

Some pollutants have been designated as priority *hazardous* substances (PHSs) due to their toxicity, their persistence in the environment and bioaccumulation in plant and animal tissues, or an equivalent cause for concern. The cessation or phase-out of discharges, emissions and losses of PHSs to the aquatic environment is required within 20 years of the date of the adoption of measures. Related to this, the Directive also requires each Member State to establish an inventory of emissions,

discharges and losses for each river basin district or part of a river basin district in its territory. This inventory is to address both diffuse and point source emissions of all PSs. Industrial emissions will be a fundamental part of the inventory and, as such, reporting under E-PRTR can provide an important component. Improved reporting of emissions to water will, however, be required under E-PRTR for a number of chemicals.

For substances identified as being of concern at local, river-basin or national level (known as river basin specific pollutants) but not as a PS or PHS at EU level, standards are set by national governments and the results of monitoring are considered in the assessment of ecological status under the WFD. Thus far, relatively little information has been reported with respect to the specific pollutants within the RBMPs. In Germany, however, EQSs have been set for a range of specific pollutants (UBA, 2010).

The WFD objective of good groundwater chemical status is directly supported by the Groundwater Directive (GWD), which has established EU-wide groundwater quality standards for two groups of pollutants (nitrates and pesticides). However, for other pollutants, the establishment of standards at Community level has not been adopted, due to the inherent high natural variability caused by hydrogeological conditions, background levels, pollutant pathways and interactions with different environmental compartments. Consequently, for these other pollutants, the GWD requires Member States to establish their own groundwater standards, to be set as threshold values.

These thresholds are primarily based on two criteria, which respectively address the protection of associated aquatic ecosystems and groundwater-dependent terrestrial ecosystems, and the protection of water used for drinking and other purposes. To date, the thresholds established for some pollutants (e.g. arsenic, cadmium and mercury) vary markedly between Member States (EC, 2010a). In 2013, the European Commission is obliged to undertake a review of information reported under the GWD and identify whether additional pollutants should be regulated at EU level.

5.4   IPPC and E-PRTR

Emissions of hazardous chemicals from industrial installations and agricultural activities are regulated in the EU through the Integrated Pollution Prevention and Control (IPPC) Directive. Abatement strategies

implemented under the IPPC Directive have led to reductions in metal emissions to both water and air.

The Directive is based on several principles:

1) an integrated approach whereby permits account for the whole environmental performance of a plant including emissions to air, water and land, generation of waste, use of raw materials and energy efficiency,

2) the dependence of permit conditions upon implementation of best available technologies (BATs),

3) flexibility, enabling licensing authorities to account for the technical characteristics of the industrial plant, its geographical location and local environmental conditions,

4) public participation and transparency including access to permits and results from the monitoring of releases as reported under the European Pollutant Release and Transfer Register (E-PRTR).

The register implements, for the European Community, the UNECE PRTR Protocol to the Aarhus Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters. Besides the requirement to report data on industrial emissions including wastewater treatment plants, E-PRTR is to now also contain information on diffuse releases to water. In 2007, the European Commission proposed a new directive on industrial emissions integrating seven existing directives, including the IPPC Directive, into a single legislative instrument, streamlining permitting, reporting and monitoring requirements.

5.5   Sustainable use of pesticides

The thematic strategy for the sustainable use of pesticides provides a framework for minimising the hazards and risks to health and the environment stemming from the use of pesticides. Some of the measures contained in the strategy can be integrated into existing policy and legislation, but for others, this is not possible. These measures form the basis of a new framework directive 'to achieve a sustainable use of pesticides'.

The Pesticides Framework Directive (2009/128/EC) contains a number of rules, including the establishment of national action plans to set objectives

in order to reduce hazards, risks and dependence on chemical control for plant protection. Source control measures have been identified that will result in a reduced use of pesticides, including the encouragement of low-input or pesticide-free cultivation, prohibition of aerial spraying under certain circumstances, and the definition of areas of significantly reduced or zero pesticide use in line with measures taken under other legislation, for example the Habitats Directive. In addition, the potential to reduce the amount of harmful active substances by substituting them with safer alternatives is also recognised.

Furthermore, the legislation identifies specific measures to protect the aquatic environment from pesticide pollution and thus supports the WFD. These measures aim to attenuate pesticides along their transport pathways and include vegetated buffer strips adjacent to water courses — research studies indicate that such measures can lead to substantial reductions in pesticide concentrations in surface waters (for example as shown in the Footprint study). In addition, substantial reductions in pesticide use have been shown to be possible with little or no impact upon profitability or productivity. This is achievable, for example, through modification of crop rotations and sowing dates, and through the selection of more pest-resistant crop varieties. Implementation of the Pesticides Framework Directive is required to support the attainment of good chemical status under the WFD, although national legislation also has a role to play in limiting pesticide levels. Denmark's green growth action plan, for example, has set a limit for the frequency with which pesticides are applied to agricultural land.

Complementing the strategy and the Framework Directive, Regulation (EC) 1107/2009 provides harmonised, strict rules for the authorisation of plant protection products, including the requirement for risk assessments for effects on human health and the environment to be carried out before a product can be placed on the market.

5.6 Marine Strategy Framework Directive

The Marine Strategy Framework Directive (adopted in June 2008) was introduced to protect Europe's marine environment more effectively. It aims to achieve good environmental status of the EU's marine waters by 2020 and to protect the resource base upon which marine-related economic and social activities depend. In September 2010, the European Commission adopted a decision outlining

the criteria necessary to achieve good environmental status for Europe's seas (EC, 2010c). Two of these relate directly to chemical pollution. Descriptor 8 of the Decision requires that concentrations of contaminants including the PSs of the EQSD be at levels not giving rise to pollution effects. Descriptor 9 specifies that contaminants in fish and other seafood for human consumption may not exceed levels established by EU legislation or other relevant standards.

5.7 Regional Sea Conventions

Both OSPAR and HELCOM have strategic objectives of preventing pollution of each convention area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment that approximate background values for naturally occurring substances and lie close to zero for man-made synthetic substances.

5.8 Substance-specific legislation

Aside from the Pesticides Framework Directive, a wide range of legislation — specific to a particular substance or group of substances — has been implemented in the European Union to protect human and environmental health. Examples include legislation relating to the production, use and disposal of PCB, which has resulted in declines in concentrations found in marine biota (HELCOM, 2010). A similar outcome has resulted from the banning of TBT in anti-fouling paints, although high levels in marine sediments can still be observed in certain locations (HELCOM, 2010). Numerous other examples exist, such as directives restricting certain hazardous substances in electrical and electronic equipment and the subsequent disposal and recycling of such equipment, controls on the marketing and use of nonylphenols, regulations on the use of biocides and, very recently, a ban on the use of bisphenol A in infant feeding bottles.

Marketing authorisation for human medicinal products requires that an environmental risk assessment be undertaken, in accordance with directives established in 2001 and subsequently amended in 2004. However, the results of this assessment are not considered in the risk-benefit balance that is the basis of the authorisation. Moreover, products authorised before 2004, such as ibuprofen, which is widely detected in surface water, did not have to undergo an environmental risk assessment. The Directive also

calls for appropriate collection systems to be set up for medicinal products that are unused or have expired. Such systems, however, do not appear to have been implemented in a suitable way in all Member States. A recent regulation (EC 1235/2010) on pharmacovigilance with regard to medicinal products for human use identifies the pollution of water and soils with pharmaceutical residues as an emerging problem for which the Member States should consider measures to monitor and evaluate the risks of environmental effects, including those which may have an impact upon human health.

An environmental risk assessment has been required for all new veterinary medicinal products since the mid-1990s. Recently, manufacturers of generic medicines have also been required to assess the environmental risk of their products, and therefore information on older compounds is increasingly becoming available. Guidelines describing how the environmental risks of veterinary products should be assessed have been produced (CVMP, 2007). The approach used in Europe is a two-phase process. In phase 1, the potential for the environment to be exposed to the veterinary product is determined. For compounds that do not pass the phase 1 check, information on their effects on terrestrial and aquatic organisms is required. Recommended aquatic studies include acute toxicity studies on daphnia and fish, with mortality as the test endpoint, and short-term studies of the effects of the compound on the growth of green or blue-green algae.

Aside from specific European legislation, internationally binding instruments have been established. They include two instruments that address the reduction and/or elimination in production, use and release of persistent organic pollutants (POPs): the Aarhus Protocol on POPs and the Stockholm Convention on POPs.

6 Improved assessment and modelling tools

Assessments of the levels and effects of hazardous substances in the aquatic environment are complicated by an underlying dilemma. A focus upon determining the concentration of a few pre-selected PSs bears a strong risk of missing other important (including emerging) problematic substances. In addition, such an approach disregards the effects of chemical mixtures and interactions with other stressors, thereby further diminishing the likelihood of reliably linking cause with biological effect. However, it is neither practical nor affordable to sample and analyse at sufficient spatial and temporal resolution for hundreds of individual substances within fresh and marine waters, including the water column, sediment and aquatic biota.

To improve this situation, recent European research studies (e.g. Modelkey) have led to the development and testing of new assessment and modelling tools that help to link chemical contamination with observed deterioration of ecological quality in freshwater ecosystems. Such tools include innovative approaches to the evaluation of existing chemical and biological monitoring data, together with site-specific experimental techniques to establish cause-effect relationships.

For example, the 'Species at risk' (SPEAR) index (Liess and von der Ohe, 2005), a novel, stressor-specific indicator for the presence of invertebrate species sensitive to organic toxicants in an aquatic ecosystem, helps to diagnose toxic stress in aquatic communities even in the presence of other stressors. It has been shown for different river basins that the reduction of SPEAR, reflecting for example the disappearance of benthic invertebrates, is correlated with increasing contamination expressed as toxic units based on the toxicity to *Daphnia magna* as a standard test organism (Figure 6.1; von der Ohe et al., 2009). The relationships derived also capture the impact of confounding factors such as the recovery potential due to non-impacted upstream sites that allow for the re-colonisation of affected water bodies. The toxic unit approach is based on concentration addition as a widely accepted model for mixture toxicity and considers the whole range of monitored compounds. Both the SPEAR index and the toxicity units approach are generally applicable to biological and chemical monitoring data, respectively, with the latter addressing the reality of exposure to

mixtures in the aquatic environment. At present, a SPEAR index for organic toxicants and pesticides has been established and validated; however, several new indices specific to other stressors are under development.

Where no toxicity data for monitored substances are available, quantitative structure-activity relationship (QSAR) models help to fill the gaps (von der Ohe et al., 2011), correlating biological activity with chemical structure. As an alternative approach, the effect and probable cause (EPC) model may be applied to estimate deviations of communities from a reference situation (i.e. where there is an absence of significant human disturbance or alteration) and the contribution of different stressors to this effect (de Zwart et al., 2009; Posthuma and de Zwart, 2006). Toxic contamination is translated to multi-substance 'potentially affect fractions' (msPAF) based on mixture toxicity and species sensitivity distributions. Thus msPAF reflects an estimate of

Figure 6.1 **Relationship between the presence of sensitive species expressed as SPEAR and the contamination expressed as the sum of toxic units (TUs) towards *Daphnia magna* as the reference organism**

SPEAR (%)

Log TU$_{Sum}$ *Daphnia magna*

● Sites with recovery potential
○ Sites without recovery potential
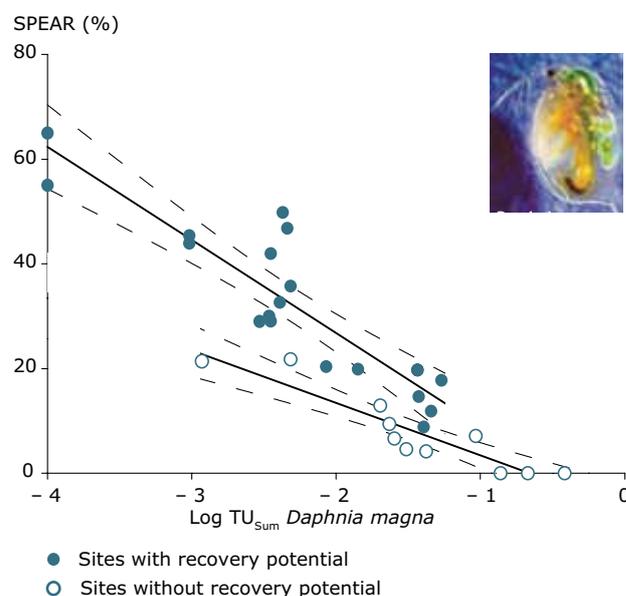
Source: Liess and von der Ohe, 2005.

the number of species that will be lost due to the measured contamination. The EPC model enables the relative contribution of different causes (multiple stressors) of the loss of species to be quantified in a river basin.

For the estimation of downstream risks of pollution from point discharges, a generic exposure model widely applicable to river basins has been developed (van Gils et al., 2009). It establishes spatial relations between pollution sources and ecological risks taking into account the geometry, hydrology, and fine sediment dynamics of European river basins. In addition, the model accounts for bio-accumulation and biomagnification, so that impacts up to the level of top predators (secondary poisoning) can be assessed.

For the identification and confirmation of toxic effects and individual toxicants as the cause of these effects, a number of experimental tools are available. These are valuable, for example, where the chemical status of a water body is apparently classified as 'good' in terms of PSs and EQS, but where biological quality is known to be poor. In other words, in locations where it remains unclear as to whether one or more non-PS (of which there may be hundreds in an individual sample) are a causal factor.

Numerous *in vitro* and *in vivo* assays together with a set of biomarkers are available for trophic level or mode-of-action related identification and assessment of effects. These tools can be used, therefore, to verify that chemicals are a causative factor in the observed biological deterioration. If the assays do not verify chemicals as a causal factor, non-chemical stressors are likely to be primarily responsible for the biological deterioration and further assessment can be focused in this direction. If, however, a chemical cause is established, effect-directed analysis (EDA) of relevant toxicants combines the bioassays with fractionation and chemical analysis as well as structure elucidation to determine the underlying causes, including previously unsuspected chemicals contributing to the effects of the complex mixture (Figure 6.2; Brack, 2003). Selection of sites representative of a river basin is important with respect to the EDA approach; ideally, sampling should occur downstream of major sources of pollution but also in integrative sinks such as reservoirs, harbours or estuaries, particularly for sediment-associated substances.

Application of EDA to sediment extracts from major European rivers suggests that the role of semi-polar and polar compounds has, to date, been significantly underestimated in sediment risk assessments focused on metals and non-polar compounds such as PAHs, PCBs and chlorinated pesticides (Lübcke-von Varel et al., 2011). EDA focusing on algal growth inhibition, mutagenicity, tumour promotion and endocrine disruption as endpoints has suggested a clear dominance of polar fractions causing these effects. The attribution of impacts to more polar compounds was strengthened when bioavailability was considered in the analysis. This has been shown, for example, for the biocide triclosan, which is used in many personal care

Figure 6.2   Scheme of effect-directed analysis
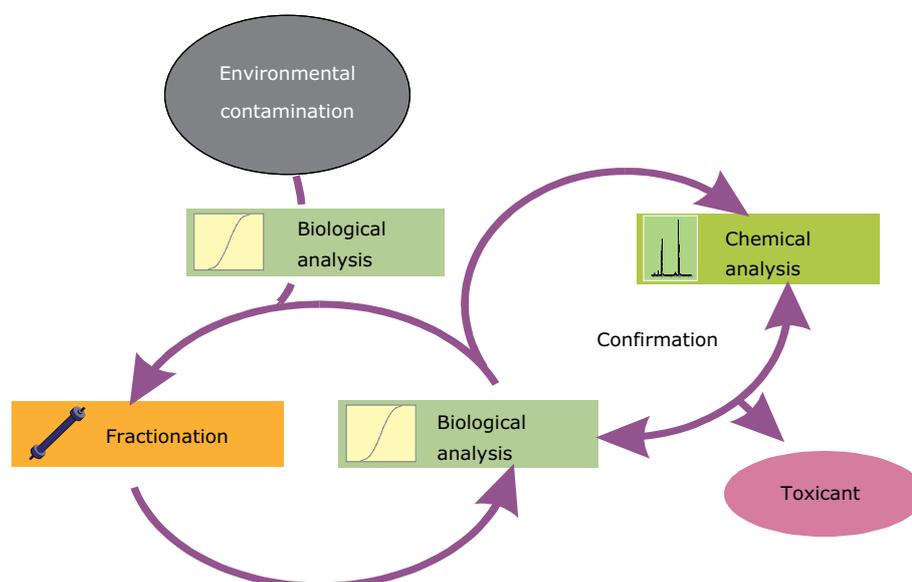
Source: Brack, 2003.

products and released via wastewater treatment plants. Triclosan has been identified as a major toxicant to green algae in contaminated sediment despite the co-occurrence of great concentrations of PAHs and other classical sediment contaminants (Bandow et al., 2009).

EDA has been particularly successful in identifying endocrine disrupters such as oestrogenic (Thomas et al., 2001) and androgenic compounds (Thomas et al., 2002; Weiss et al., 2009a). Natural oestrogenic steroids together with the synthetic contraceptive pill component 17α-ethinylestradiol discharged primarily from wastewater treatment plants have been identified by EDA as major oestrogens in water samples and fish bile (Houtman et al., 2004; Thomas et al., 2001). Based on these findings, these compounds were taken into consideration in monitoring, risk assessment and technological improvements for wastewater treatment plants. Other examples include the identification of naphthenic acids as important *in vitro* xeno-oestrogens and anti-androgens in offshore-produced water discharges (Thomas et al.,

2009) and of poly-aromatic oxygen and sulphur heterocyclic compounds causing dioxin-like effects in sediments (Brack and Schirmer, 2003).

Confirmation of compounds identified in environmental samples as the likely cause of adverse effects on aquatic organisms and communities may be provided through the use of cause-effect chains (Figure 6.3). In Modelkey, a range of tools has been compiled, advanced and tested for this purpose in case studies (Hein et al., 2010). These notably include *in vitro* assays on new toxicological endpoints such as endocrine disruption of the thyroid hormone transport protein transthyretin (Weiss et al., 2009b), biomimetic tools for bioavailability assessment (Sormunen et al., 2010), *in vivo* biomarkers (Wenger et al., 2010), and pollution-induced community tolerance (PICT) approaches (McClellan et al., 2008). Whole exposure-effect chains have been established for example for endocrine disrupters. These range from *in vitro* effects, *in vivo* effects on snails in the lab and *in situ* caging experiments to changes in the community (Schmitt et al., 2010a, 2010b and 2011).

Figure 6.3   Exposure effect chain to confirm chemical contamination as a cause of deteriorated ecological status
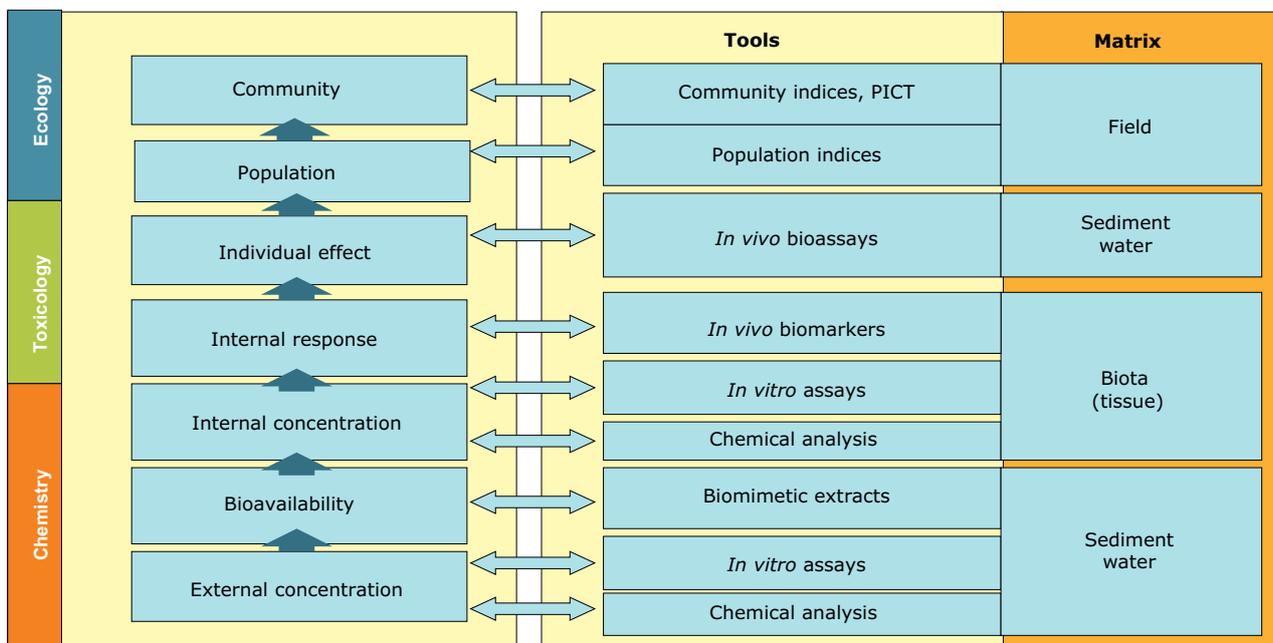
Source: Modelkey.

7 Conclusions

7.1 Hazardous substances in water affect aquatic life and pose risks to human health

Many studies have documented a range of detrimental impacts of hazardous substances upon freshwater and marine biota. These effects manifest themselves at molecular, cellular, tissue, organ and ecosystem level. Such impacts diminish the services provided by aquatic ecosystems, and consequently the benefits, and notably the revenue, which can be derived from them. Human exposure to hazardous substances can occur via water, through the consumption of contaminated fish and shellfish and through the ingestion of contaminated drinking water. The exceedance of regulatory levels in seafood is documented for several hazardous substances in Europe's seas.

7.2 Legislation continues to play an important role, but challenges exist

A wide range of legislation has been implemented to address the chemical quality of Europe's fresh and marine waters, both directly and indirectly. Collectively, this legislation encompasses a wide range of measures and approaches.

Established legislation has produced clear positive outcomes. Abatement measures introduced by the IPPC Directive, for example, have led to reduced metal emissions, and legislation relating to the production, use and disposal of PCBs has resulted in declines in concentrations found in marine biota. A similar outcome has resulted from the banning of TBT in anti-fouling paints due to its endocrine-disrupting impacts on marine invertebrates, although high levels in marine sediments can still be observed in certain locations.

The implementation of more recent legislation, such as REACH, the EQSD and the Pesticides Framework Directive, is likely to play a key role in strengthening the protection of both human health and aquatic environments. However, despite the comprehensive suite of legislation adopted in Europe, some important challenges remain. These are briefly highlighted in the following subsections.

7.3 The potential risks posed by emerging pollutants are insufficiently understood

The known persistence, bioaccumulation and toxicity of a number of hazardous substances mean that they are addressed by various pieces of European legislation, notably through classification as a PS or PHS under the EQSD. However, for a range of emerging pollutants, the awareness of potential effects has developed only recently and remains incomplete. These emerging pollutants include substances that have existed for some time, such as pharmaceutical products and personal care products, but also relatively new substances, such as nanomaterials.

Information regarding emerging pollutants is relatively scarce, both regarding their concentrations and their effects in the aquatic environment — an observation which reflects the fact that emerging pollutants are not, typically, included in routine monitoring programmes. This gap creates a conundrum. Unless a substance is regulated, widespread monitoring is unlikely to be undertaken. However, without such monitoring data, the risks to the aquatic environment and to human health cannot be robustly assessed, limiting the justification for regulation, particularly given the expense associated with monitoring and analysis. More information is needed, therefore, with respect to emerging pollutants, to build on the data provided by existing initiatives such as the JRC monitoring programme and the Norman network, to better identify those that pose significant risk to environmental and human health. Research studies must continue to play an important role in this respect. However, these do not necessarily provide Europe-wide information at a sufficient temporal and spatial scale. To support the identification of substances for prioritisation under the EQSD, a targeted EU-wide approach is therefore also desirable.

7.4 The ubiquity of some hazardous substances presents particular challenges

Certain hazardous substances, including mercury, TBT and PAHs, can be described as persistent, bioaccumulative and toxic, occur widely in

the environment, and have well documented detrimental effects upon both environmental and human health. Typically, their danger has been known for some time and has led to the implementation of strong regulation, with reduced emissions to air and water being recorded. However, their persistence and ubiquity, particularly in sediment and biota, mean that they continue to pose a risk to aquatic environments and that natural recovery may take decades (e.g. with respect to TBT in coastal sediment and biota). As a result of long-range transport in the atmosphere, some of these substances have contaminated water bodies in remote regions far from human activity (e.g. PAHs in mountain lakes).

Overall, these various factors present a significant challenge with respect to the regulation of such substances under the WFD and the EQSD. Remediation of highly contaminated hotspots may be possible if technically and economically feasible, but options are limited where strong legislation is already in place. Moreover, such substances are often hydrophobic and tend to accumulate in sediment and biota. As a result, their concentrations in these matrices are likely to be higher, and therefore more detectable and measurable than in water. This difference means that Member States that apply a water column EQS for such hydrophobic substances can underestimate their risk to the aquatic environment. If different matrices are used in different locations, the results may not be comparable. Inconsistencies in the matrix used are known to have led to unrepresentative differences in the reporting of chemical status in the RBMPs of different Member States.

7.5 The quantitative understanding of sources and emissions must be improved

Information regarding the sources and emissions of many hazardous substances remains incomplete, limiting the scope to identify and target appropriate measures. The EQSD requires each Member State to establish an inventory of emissions, discharges and losses for each river basin district or part of a river basin district in its territory. Inventories must cover both the diffuse and the point source emissions of all PSs. Industrial emissions will be a fundamental part of the inventory and, as such, reporting under E-PRTR can represent an important component.

However, information provided in this report and elsewhere (e.g. Greenpeace, 2010) suggests that,

for some chemicals, the reporting of emissions to water under E-PRTR is incomplete. As a result, for example, despite evidence of declining riverine metal loads, it is not possible from reported data to clearly track this trend back to reduced emissions from industrial facilities. Achieving full reporting under the PS inventory is of critical importance. This should include comprehensive quantification of emissions, enable each source to be apportioned, establish a baseline against which trends over time can be compared, and optimise the identification of measures. European research studies such as ScorePP and Socopse can support improved quantification of emissions.

7.6 Smart monitoring and assessment tools are required

It is not practical or affordable to sample and analyse at sufficient spatial and temporal resolution for hundreds of individual chemicals within fresh and marine waters, including aquatic biota and sediments. However, a focus upon a few pre-selected priority substances entails a strong risk of missing other problematic substances.

Related to this aspect is the key issue of chemical mixtures as found in the more polluted water bodies of Europe. Laboratory studies have shown that the combined effects of chemicals upon aquatic life can be additive, meaning that chemicals at concentrations which, individually, would not lead to detectable adverse effects, can result in observable detrimental effects when combined. Recent European research has led to the development of assessment tools that help to link chemical contamination with observed deterioration in ecological quality, establishing cause-effect relationships. Further development of such tools is advisable and can be achieved through European research programmes.

7.7 Chemicals should be produced and used more sustainably

Despite the comprehensive suite of legislation now implemented within Europe, the ubiquitous use of chemicals in society represents a major challenge with respect to the protection of aquatic ecosystems; emissions of hazardous substances to the environment, including fresh and marine waters, can occur at all stages of their life cycle. Whilst these emissions arise from various sources, the private and public consumption of consumer goods is a fundamental driver of the production and, therefore,

of the release of hazardous substances to the environment.

The promotion of more sustainable chemical consumption patterns for the future may be achieved most effectively through a mix of policy responses involving regulation, economic incentives and information-based instruments, including awareness-raising campaigns (EEA, 2010d). Implementing a more sustainable approach to the consumption and production of chemicals would not only benefit Europe's environment but also reduce the detrimental effects arising in other parts of the world as a result of the growing proportion of goods imported to Europe.

To help achieve a more sustainable production of chemicals, wider implementation of 'green chemistry' is required. This approach involves the development of new processes and technologies that maintain the quality of a product but reduce or eliminate the use and generation of hazardous substances. The adoption of sustainable, green chemistry techniques has been shown to generate financial benefits and hence provide competitive advantage. Currently, however, there is no comprehensive EU legislation on sustainable chemistry in place (EEA, 2010b).

7.8 Climate change will also affect chemical water quality

In the absence of appropriately strong measures, climate change is likely to adversely impact chemical water quality in a number of ways over the coming decades. Hotter, drier summers and increasingly severe and frequent droughts, for example, will deplete river flows, reducing contaminant dilution capacity and lead to elevated concentrations of hazardous substances. In regions where more intense rainfall is expected, the frequency and severity of polluted urban stormflows is predicted to increase (Nie et al., 2009; Waters et al., 2003), whilst the re-mobilisation and redistribution of contaminated sediments will become more likely (Hilscherova et al., 2007), for example as a result of floods.

More frequent intense rainfall is also likely to exacerbate the flushing of agricultural pollutants, including pesticides and veterinary medicines, to water bodies (Bloomfield et al., 2006; Boxall et al., 2009). Moreover, an increased prevalence of pests, weeds and diseases may lead to wider and more frequent application of both pesticides and veterinary medicines (Bloomfield et al., 2006; Boxall et al., 2009), although higher temperatures will increase the volatilisation of pesticides and the degradation of pesticide residues in soil and surface waters (Bloomfield et al., 2006). In the long term, land-use change driven by changes in climate may have a more significant effect on pesticides in the environment than the direct impacts of climate change on specific pesticide fate and transport processes (Bloomfield et al., 2006).

Ocean acidification, driven by increasing atmospheric CO_2, may change the speciation of metals in seawater and, therefore, their interaction with marine organisms (Millero et al., 2009). Coastal erosion, likely to be exacerbated under climate change, has led to the exposure of landfill sites in Europe, with a clear potential for contamination of coastal waters.

7.9 Training for expertise in environmental risk assessment should be supported

Investment in training is critical to ensure the ongoing availability of skilled professionals to undertake the environmental risk assessment of hazardous substances such as those presented in this report. One example with respect to human health risk assessment is the 'European toxicology risk assessment training' (TRISK) initiative, which contributes directly to the training of risk assessors across Member States, thus addressing the need for human health risk assessment capability at EU, national, and private sector levels over the longer term. A similar initiative with respect to environmental risk assessment could help to ensure greater capability across the EU in the context of assessing risks from hazardous substances in Europe's aquatic environments.

Main abbreviations and acronyms

CSO	Combined sewer overflow
EDA	Effect-directed analysis
E-PRTR	European Pollutant Release and Transfer Register
EQS	Environmental quality standard
EQSD	Environmental Quality Standards Directive
GWB	Groundwater body
GWD	Groundwater Directive
HELCOM	Helsinki Commission (the governing body of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, also called Helsinki Convention)
IPPC	Integrated Pollution Prevention and Control (Directive)
l	Litre
µg	Microgram
ng	Nanogram
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic (opened for signature at the ministerial meeting of the Oslo and Paris Commissions in Paris on 22 September 1992)
PAH	Polyaromatic hydrocarbon
PBT	Persistent, bioaccumulative and toxic (chemical)
PCB	Polychlorinated biphenyl
PHS	Priority hazardous substance
POP	Persistent organic pollutant
PS	Priority substance
RBD	River basin district
RBMP	River basin management plan
REACH	(Regulation on the) Registration, Evaluation, Authorisation and Restriction of Chemicals
t	Tonne
TBT	Tributyltin
WFD	Water Framework Directive
WWTP	Wastewater treatment plant

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Annex 1 EU projects

With respect to hazardous substances, this report refers to several key EU projects. These are:

- 'Functional tools for pesticide risk assessment and management' (Footprint)
http://www.eu-footprint.org

- 'Models for assessing and forecasting the impact of environmental key pollutants on marine and freshwater ecosystems and biodiversity' (Modelkey)
http://www.modelkey.org

- 'Network of reference laboratories for monitoring of emerging environmental pollutants' (Norman)
http://www.norman-network.net/ index_php.php?menu2=public/about_us/about_us&module=public/about_us/home

- 'Novel methods for integrated risk assessment of cumulative stressors in Europe' (NoMiracle)
http://nomiracle.jrc.ec.europa.eu/default.aspx

- 'Source control of priority substances in Europe' (Socopse)
http://www.socopse.se

- 'Source control options for reducing emissions of priority pollutants' (ScorePP)
http://www.scorepp.eu

- The 'European toxicology risk assessment training' (TRISK) initiative
http://www.trisk-project.eu

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