



Emerging pollutants in the environment: A challenge for water resource management

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Abstract

A significant number of emerging pollutants (EPs) resulting from point and diffuse pollution is present in the aquatic environment. These are chemicals that are not commonly monitored but have the potential to enter the environment and cause adverse ecological and human health effects. According to the NORMAN network, at least 700 substances categorized into 20 classes, have been identified in the European aquatic environment. In light of their potential impact action is urgently required.

In this study, we present a concept that shows the current state of art and challenges for monitoring programs, fate and risk assessment tools and requirements for policies with respect to emerging pollutants as a base for sustainable water resource management.

Currently, methods for sampling and analysis are not harmonized, being typically focused on certain EP classes. For a number of known highly hazardous EPs detection limits are too high to allow proper risk assessment. For other EPs such as microplastics method development is in its infancy. Advanced ultra-sensitive instrumental techniques should be used for quantitative determination of prioritized EPs in water, suspended matter, soil and biota. Data on EPs' and their metabolites' properties that determine their fate in the environment are often not available. National surveys on water quality often use different parameters for water quality assessment and often do not include EPs. A harmonized monitoring of surface and groundwater is not yet achieved and urgently required. Specific component integrated into models assessing the fate of EPs in a multi compartment environmental approach are missing and must be developed.

The main goal of risk assessment is the overall protection of ecological communities in the aquatic environment and human health. New methods for assessing the cumulative risks from combined exposures to several stressors, including mixtures of EPs in a multi-scale approach are required.

A combination of regulations and management measures with respect to use/emissions of EPs into the environment, as well as to their occurrence in the environment are fundamental to reach an efficient water resource management.

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1. Introduction

Water pollution is a severe worldwide problem that urgently requires concepts for monitoring and implementation plans deriving solutions. Every day, 2 Mio t sewage, industrial and agricultural waste are discharged into the world's water (UN WWAP, 2003), equivalent of the weight of the entire human population. The UN estimates that the amount of wastewater produced annually is about 1500 km³, six times more water than exists in all the rivers of the world (UN WWAP, 2003). Lack of adequate sanitation causes water resources contamination worldwide, making it one of the most significant causes of water pollution. Worldwide, 2.5 billion people live without proper sanitation (UNICEF, 2009). In some regions of the world, more than 50% of native freshwater fish species are at risk of extinction, and this is also the case for nearly one-third of the world's amphibians (Vié, Hilton-Taylor, & Stuart, 2009).

Over 70% of the people who lack sanitation, or 1.8 billion people, live in Asia. In China, which has a rapidly growing economy water is a scarce resource as just 8% of the world's fresh water has to meet the needs of 22% of the world's population. However, 33% of industrial waste water, and 70% of household sewage is untreated and directly released into rivers and lakes, while 80% of China's cities have no sewage treatment facilities and water supplies in 90% of the cities are contaminated. Environmental degradation costs China nearly 9% of its annual gross domestic product (<http://factsanddetails.com/china/cat10/sub66/item391.html>).

Nowadays, more than 700 emerging pollutants, their metabolites and transformation products, are listed as present in the European aquatic environment (www.norman-network.net). Emerging pollutants (EPs) are defined as synthetic or naturally occurring chemicals that are not commonly monitored in the environment but which have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects. In some cases, release of emerging pollutants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging pollutants (<http://www.norman-network.net>). EPs are currently not included in (inter)national routine monitoring programmes and their fate, behavior and ecotoxicological effects are often not well understood. They can be released from point pollution sources, e.g. waste water treatment plants from urban or industrial areas, or from diffuse sources through atmospheric deposition or from crop and animal production (Fig. 1). EPs are categorized into more than 20 classes related to their origin (<http://www.norman-network.net>). The prominent classes are: pharmaceuticals (urban, stock farming), pesticides (agriculture), disinfection by-products (urban, industry), wood preservation and industrial chemicals (industry). In light of the potential impact of these substances on aquatic life and human health, the lack of knowledge regarding their behavior in the environment and the deficiency in analytical and sampling techniques, action is urgently required at multiple levels.

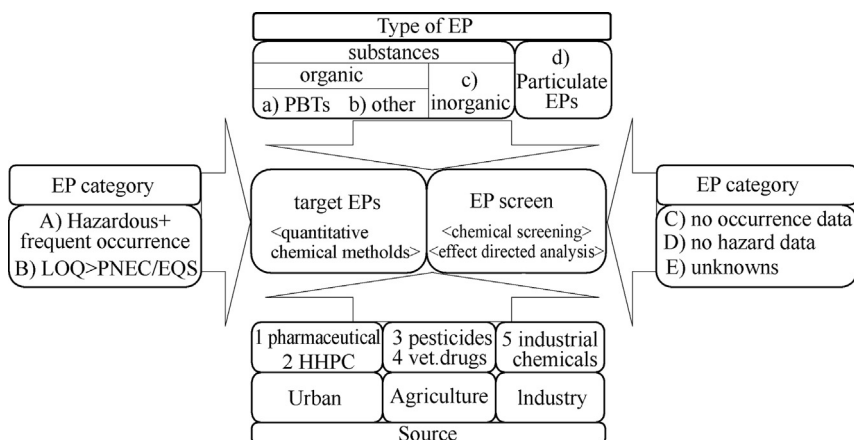


Fig. 1. Types of EPs from different origins that can be monitored by targeted and screening approaches.

(PBT=persistent bioaccumulative and toxic, LOQ=limit of quantification, PNEC=predicted no-effect concentration, EQS=environmental quality standard, HHPC=household & personal care products).

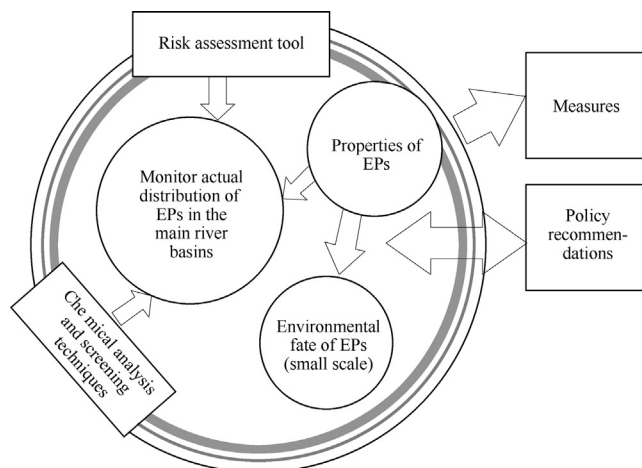


Fig. 2. Concept for management of emerging pollutants in the aquatic environment.

A new mechanism is needed to provide targeted high-quality monitoring information on the concentration of the most relevant EPs for risk assessment across the river basins. In the European Union, a watch list of EPs is elaborated from national monitoring programs, because that is required by the Water Framework Directive (Directive, 2000). This list presents emerging substances requiring further attention due to their high frequency of occurrence, the expected risk for human health and/or aquatic life, and/or for a lack of analytical techniques. The WFD (Directive, 2000) has presently designated 33 substances or compound classes for the EU as priority pollutants. How to manage these substances remains a challenge. In order to keep monitoring costs at reasonable levels, any approach or mechanism should focus on a limited number of substances.

The scope of this article is to present a concept that shows the requirements for monitoring programs, fate and risk assessment tools and requirements for policies with respect to emerging pollutants as a base for sustainable water resource management (Fig. 2).

2. Challenges for monitoring programs

2.1. Chemical analysis and screening techniques

Detection, identification and quantification of EPs and their transformation products in the various environmental compartments is essential for gaining knowledge on their occurrence and fate. This is highly challenging for several reasons: the number of currently known potential EPs (and relevant transformation products) is very high (> 700 in Europe). Their relevance changes over time due to changes in production, use and disposal of (agro)chemicals, and new information on their occurrence, fate and hazards. Certain EPs o.a. hormones, pyrethroids and certain organophosphorus pesticides (Von der Ohe et al., 2011; RIVM, 2012) affect the aquatic environment at extremely low concentrations and need analytical methods with correspondingly low detection limits. Not all EPs/TPs are known at the moment of sampling and analysis.

Different types of EPs with widely varying physical/chemical properties exist: (i) organic substances which can be subdivided in PBTs (persistent bioaccumulative and toxic substances such as POPs) and more polar substances (e.g. pesticides, pharmaceuticals, industrial chemicals), (ii) inorganic compounds (e.g. trace metals) and (iii) particulate contaminants such as nanoparticles and microplastics (Fig. 1).

Current state-of-the-art methods for sampling and analysis vary amongst monitoring laboratories. They are typically dedicated to certain EP classes and by far do not cover the full range of EPs of potential concern. Moreover, for a number of known highly hazardous EPs that are monitored, the detection limits are inadequate to allow proper risk assessment. Furthermore, for EP-types of more recent concern such as nanomaterials, microplastics, and ionic liquids, methods for sampling and environmental analysis are in the initial state or virtually non-existent (Farré, Sanchis, & Barceló, 2011; Richardson & Ternes, 2011).

In conventional methods targeting at specific EPs, advanced ultra-sensitive instrumental techniques (e.g. GC-APCI-MS/MS, latest generation LC-MS/MS) have become available but so far they are hardly used for routine monitoring. The application of such technologies would simplify sample preparation, offer improved possibilities for simultaneous determination of multiple EPs, and/or significantly improve detection limits for EPs with very low PNECs. Although higher in costs, the use of such instruments would be highly beneficial for quantitative determination of prioritized EPs in water, suspended matter, soil and biota.

Conventional methods measure only *a-priori* selected EPs. In recent years generic chemical screening approaches based on chromatography with full scan mass spectrometry have become increasingly popular to complement or replace existing targeted methods (Hernández et al., 2012). In contrast to conventional targeted methods, the sample is analyzed in a comprehensive way and in essence one can decide afterwards which EPs of interest to retrieve from the raw data. This is an effective way of screening samples for very high numbers of EPs and an economical way to pick up unexpected EPs for which application of quantitative targeted methods with all associated analytical quality control is not justifiable. Other important advantages are the ability of retrospective detection of additional EPs without the need for re-sampling/re-analysis of the sample, and detection and identification of unknowns. A hurdle still to be taken to fully benefit from the potential of this technology in routine practice is the availability of adequate data processing software and associated databases.

2.2. Properties and behavior of emerging pollutants

Occurrence of EPs can result from point (mainly urban and industry) or diffuse (agriculture) pollution. The transport of EPs from diffuse sources to the sink (water bodies) strongly depends on the EPs properties (Farré et al., 2010; Geissen et al., 2010) such as volatility, polarity, adsorption properties, persistence and the properties of the interacting compartments. EPs from urban or industrial waste water treatment plants are directly discharged into rivers where their environmental fate is of concern (degradation, sorption at the sediment, transport in the aqueous phase). EPs can undergo significant biodegradation and transformation in effluent-impacted surface waters and groundwater. Biodegradation depends on the presence of a community of organisms able to transform the contaminants through metabolic networks and the bioavailability of contaminants, especially in sediments and soil. The natural biodegradation can vary significantly between compounds and has not been specifically studied for many EPs like hormones, detergents and pharmaceuticals (Bradley, Barber, Kolpin, McMahon, & Chapelle, 2008). The most desirable approach for realistic biodegradation simulation tests is using experimental systems that approximate real environmental conditions as much as possible. Intermediates and/or end-products of the photodegradation of EPs may also exhibit properties which appreciably affect the living environment (Xie et al., 2012).

In rural areas, EPs are diffusely spread over the area and undergo transport by air, runoff, erosion or leaching until reaching a water body. Properties such as adsorption behavior of pharmaceuticals for example can vary vastly in different soil types because they occur in both ionized and un-ionized form, which affects their interaction with different compounds in the soil (ter Laak, Agbo, Barendregt, & Hermens, 2006). The presence of manure or sludge in agricultural soils can affect not only the sorption behavior of these materials but also their persistence (Monteiro & Boxall, 2009). The environmental behavior of engineered nanomaterials (ENM) is largely unknown. Transformations of ENM before and after entry to the environment, such as surface modification by humic acids, interactions with common cations, and dissolution under natural conditions, may be important in controlling transport and fate, and require further research (Kasel et al., 2013a, b; Liang et al., 2013). Their behavior is different than that of non-particulate contaminants, so new paradigms will be needed for ENM in water, soil, sediment and biota. Research is needed in this area to produce information that can be used to develop, refine and calibrate models for studying EPs.

2.3. Multi compartment monitoring at river basin scale

Numerous data from national or river basin scale surveys on water quality are available, however taking different parameters for water quality assessment under consideration and often do not include emerging pollutants. A harmonized monitoring of surface and groundwater is not yet achieved for many EPs in most of the countries of the world (Hanke, Mariani, Comero, Loos & Bidoglio, 2012). Little information is available on the dynamics of EPs in between the water column, sediments and the accumulation in the aquatic food chain, and on the loads from the agro environment through diffuse pollution or from urban and industrial areas via point pollution. The Norman group

started to collect data from national reports to get an overview of the occurrence of EPs in Europe (www.normandata.eu). Although this is a good starting point, data lack a framework for harmonized sampling and analytical methods. Furthermore, detection limits for numerous EPs are above the respective PNEC, so false negative results are expected. Consequently the quantification of risks for man and the environment arising from this group of chemicals – the prerequisite for making well balanced environmental policies – remains fragmented.

In Europe, some monitoring activities describe the presence and fate of EPs in some of the interconnected compartments well. However, due to the variety of research approaches, the differences in data acquisition (including planning and sampling), and the temporal/seasonal incoherence of the experiments, the data cannot be interpreted at a large scale. Even the most sophisticated data bases cannot resolve the lack of a harmonized approach in acquiring and even interpreting those data.

The few monitoring exercises executed at a larger scale, such as the river basin wide international exercises in the Danube (Umlauf et al., 2008) or Elbe Rivers (Umlauf, Stachel, Mariani, & Goetz, 2011) for water, the EMEP network for ambient air, or the LUCAS soil survey (Gallego, Pinilla, & Bamps, 2008; Tóth, Jones, & Montanarella, 2013) are mono compartmental, driven by the policies made for a single environmental compartment. But EPs, as many other toxicants, display a multi compartmental presence in the environment. Mono compartmental policies and the associated compliance monitoring schemes cannot provide the full picture on the exchange and transformation dynamics between all compartments concerned, including the food chain. Consequently, EP risk management remains fragmented and static.

An effective mechanism for a river based assessment and management of the risk that EPs pose to man and the ecosystem through the development and application of harmonized methodologies applied to all prominent compartments containing EPs, with particular emphasis of prioritization in the aquatic environment is required. An optimized sampling strategy ensures the requirements for spatial and temporal resolution while minimizing the effort for data acquisition.

3. Challenges with respect to tools modeling the fate of emerging pollutants

Modeling frameworks are poorly developed for EPs' fate – with the exception of pesticides – in the soil–water environment and require further development. The challenge is to model transport and fate of various EPs from all possible sources (urban, industrial, agriculture), through catchments to their outlet (Fig. 2). EPs from diffuse sources are transported via the soil–water system to the sink (water body) (McGuire & McDonnell, 2006). Depending on their properties, EPs can be transported by different processes, such as by runoff, erosion or leaching and enter into groundwater or surface water. They may be intercepted by the soil through adsorption or can be degraded during the transport and never reach the water bodies. Once water bodies are reached, further transport downstream in solution or attached to suspended material may occur. As EPs are “emerging”, little experimental evidence is available on their transport and partitioning in catchments – and models to simulate this transport have not been parameterized for EPs except for pesticides.

There is a need for investigation of the reactive transport at different scales. Various models are available for calibration, validation, and process understanding, particularly in the context of pesticide fate screening, and that are all based on similar basic principles as one dimensional unsaturated water flow in soil, where the EP behaves as an adsorbing and degrading solute (MACRO, GEOPEARL, FOCUS, SWAP-ORCHESTRA) (Tiktak, Nie, Linden, & Kruijne, 2002; Tiktak, De Nie, Piñeros-Garcet, Jones, & Vanclooster, 2004; FOCUS, 2009; Schotanus et al., 2014). As they derive from pesticide screening, specific processes that may occur for a certain class of EPs are usually not incorporated in such models. Examples of emerging processes are small or nano-particle accumulation at soil water/air interfaces, coating-formation, and interactions between different EPs. A major unknown, in parameterization, is whether complex interactions should be considered to be time-dependent, or not.

As the EP fate modeling usually has the focus on the catchment scale, the transfer of water, particles, and chemicals across interfaces between the soil, groundwater, and surface water compartments needs to be taken into account. These interfaces (groundwater level, hyporheic zone) are physically, chemically and biologically highly complex zones, of which it is recognized that they are generally investigated in a highly simplified manner. The flow equations are different for the unsaturated soil, saturated groundwater and surface water. Hence, consideration of two or three of these zones introduces conceptual and software complexity that is not always compatible with common software (e.g. MODFLOW-MT3D/RT3D, or GIS-type extensions such as SWAT, GEOPEARL) (Tiktak et al., 2002;

Zheng, Hill, Cao, & Ma, 2012; Yalaw, van Griensven, Ray, Kokoszkiwicz, & Betrie, 2013). An example of multicompartiment software is HydroGeoSphere (Therrien, McLaren, Sudicky, & Panday, 2010). Such versatile software comes, however, at a price as it may be computationally very demanding (Van der Velde, Torfs, van der Zee, & Uijlenhoet, 2012).

With parameterized models, catchment scale transport and accumulation of EPs, under varied meteorological forcing, land use and EP-release scenarios and EP forcing can be assessed (Zheng et al., 2012). At larger scales than relatively small sub-catchments, such an approach breaks down due to its computational and data demand (Brunner & Simmons, 2012). As an alternative approach for such situations the model concept of the Travel Time Distribution (TTD) was formulated (Botter, Bertuzzo, & Rinaldo, 2010). This approach focuses on the main features and robust descriptors of the main pathways and the storage compartments within a (sub)catchment. The TTD concept is based on the recognition, that between the soil surface and the catchment outlet, there are many different pathways, each with their own dynamics, processes, and retention times for water and for chemicals. The entire collection of these pathways can be characterized by a distribution (TTD) (or histogram) of the travel times, of water and chemicals (such as EPs), between soil surface and outlet (Van der Ploeg et al., 2012).

To understand how the TTD depends on the geohydrology, and climate, several important advances have been made (Botter, Bertuzzo, & Rinaldo, 2011; Rinaldo et al., 2011). Despite these advances, the TTD approach needs further development to be applicable for EPs as it has been applied to few substances so far (Benettin, van der Velde, van der Zee, Rinaldo, & Botter, 2013). Much understanding could be gained by using the experimental data, per catchment, plus modeling with e.g. GEOPEARL, or HydroGeoSphere, to fit the TTD for a series of meteorological years, and EPs of different properties. This fitting will give information on how the discharge and chemical fluxes at the outlet are related to EP emissions under certain meteorological conditions, for sub-catchments. In other words, for a given catchment, model simulations provide the discharge and chemical fluxes at the outlets, which can then be post-processed to infer the distributions of travel times for EPs in the aquatic bodies.

4. Challenges with respect to risk assessment tools

The main goal of risk assessment is the overall protection of not only the ecological communities in the aquatic environment but also the human health of people living in contact, either directly or indirectly, with water (e.g., drinking water consumption, dietary intake of foods irrigated with water). In the past, the procedure for assessing the ecological risk of a substance consisted basically of comparing its concentrations in environmental compartments (predicted environmental concentration, PEC) with concentrations below which unacceptable/adverse effects on organisms will most likely not occur (predicted no effect concentration, PNEC) (Lepper, 2002). However, this procedure has significant difficulties, e.g. how to deal with the different PNEC values reported for a single species. The approach for human health risk assessment is slightly different, as human exposure through different pathways is estimated, prior to the comparison with threshold levels of non-carcinogenic and carcinogenic risk (reference doses and slope factors, respectively). In this framework, risk assessment usually depends on the robustness and quality of databases, as toxicity and ecotoxicity endpoints may differ depending on the sources of literature. Therefore, for an accurate evaluation of ecological and health risks, including human exposure, uncertainty and variability aspects must be considered as essential. In recent years, Intelligent Testing Strategies (ITS) have become increasingly employed by the scientific community and considered as viable tools for studying chemical substances, with a clear cost reduction and animal testing minimization. Components of ITS include the integration of a series of complementary methodologies, such as Quantitative Structure-Activity Relationships (QSARs), read-across models (or chemical categorization), thresholds of toxicological concern, exposure information, in vitro testing methodologies, as well as other in silico (or computational) models. This integration favours the minimization of weaknesses and of strengths of each one of the methodologies.

Recently, the development of physiologically based pharmacokinetic (PBPK) models has increased considerably. PBPK models are used to describe the biodistribution (intake, distribution, metabolism, and excretion) of chemicals in animals and humans (Fàbrega, Kumar, Schuhmacher, Domingo, & Nadal, 2014). In turn, new efforts have been made in order to consider possible adverse health effects of exposure to pollutant mixtures, rather than to single chemicals (Nadal, Kumar, Schuhmacher, & Domingo, 2006). The comparison of substances, as a first step to evaluate the chemical aggregation, has sometimes been executed by applying different prioritization schemes (Von der Ohe et al., 2011; Fàbrega et al., 2013), usually based on ranking and scoring systems. As a step beyond,

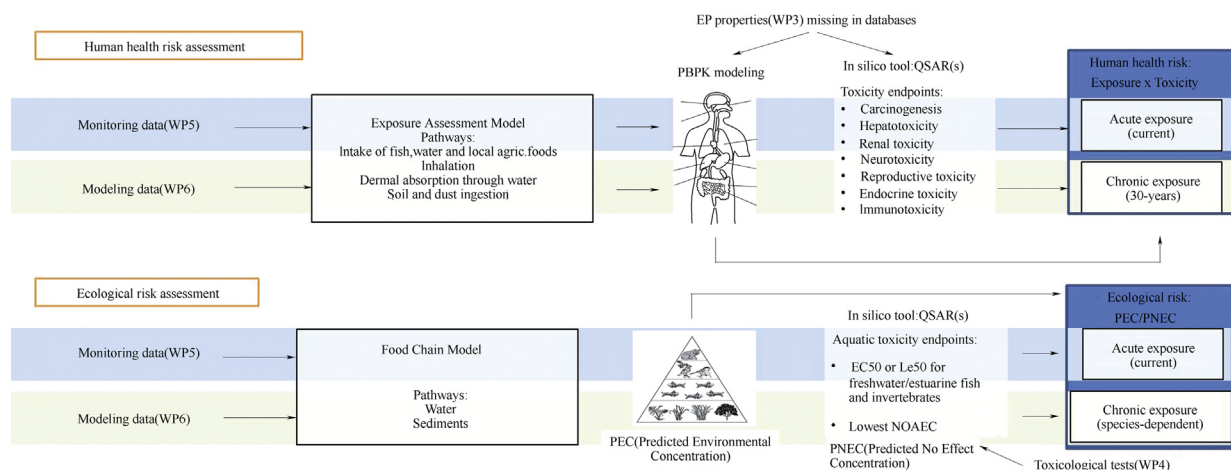


Fig. 3. Multi-scale assessment of the ecological and human health risks derived from the acute and chronic exposure to EPs contained in surface water.

uncertainty and variability aspects, inherent to data, have usually been considered using probabilistic and possibilistic approaches (Nadal, Kumar, Schuhmacher, & Domingo, 2008). Prioritization methods are essential to identify the hazards of metabolites and transformation products in comparison to their parental compounds. Consequently, they are essential to quantify the risks to human health and the environment of chemical mixtures. They form the basis to develop new methods for assessing the cumulative risks from combined exposures to several stressors, including mixtures of chemical and physical/biological agents. The multi-scale approach is presented in Fig. 3.

5. Challenges for water resource management and policies

The relevant regulatory frameworks affecting EPs in the European environment include a complex set of regulations governing the placing on the commercialization, use and emissions into the environment, and the presence of pollutants in the environment and the drinking water (quality standards/monitoring). The combination of regulations and management measures is fundamental to reach efficient water resource management.

Taking the regulations of the European Union as an example, the REACH regulation registers, evaluates, authorizes and restricts the use of nearly all chemical substances manufactured or imported into the EU (Regulation EC No 1907/2006). In terms of chemical use and emissions, agricultural activity is one of the most important contributors of diffuse pollution in Europe and emissions are predicted to increase in the future, making it a key area for regulating chemical use and emissions into the environment. The Sustainable Use Directive (Directive, 2009) addresses plant protection products. With respect to point source pollution, several directives and regulations are relevant: the Industrial Emissions Directive (IED) (Directive, 2010), the European Pollutant Release and Transfer Register (E-PRTR) (Regulation EC No 166/2006), the (Regulation EC No 1107/2009) concerning the placing of plant protection products on the market and the Urban Waste Water Treatment Directive (UWWTD) (Council Directive, 1991). Finally, regulating the presence in the environment, the Water Framework Directive (WFD) (Directive, 2000) provides a safety net, including identification and monitoring, and a list of priority substances for which concentration limits are defined in the Environmental Quality Standards Directive (EQSD) (Directive, 2008).

These regulations are the legislative base for an efficient water resource management. The specific measures can be selected for each (sub)catchment taking under consideration management options evaluated through computer simulations which will provide a quantitative evaluation of their effectiveness in reducing environmental concentrations and risks in large-scale catchments for specific EPs. This will require (1) selection of a subset of measures according to the interest of simulations in comparison to existing knowledge; (2) translate the selected measures into modeling scenarios for the tools (3) run the models, analyse the results and estimate the uncertainties; (4) comparatively assess the management measures for risk reduction. Furthermore, cost-benefit analysis should be carried out to analyse the economic feasibility of the selected measures.

The combination of regulations, use of monitoring data and application of tools for risk assessment enables the elaboration of sustainable water resource management taking under consideration the economically possible solution.

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