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The importance of indicators in monitoring water quality according to European directives

Importanza dell'utilizzo di indicatori per il monitoraggio della qualità dell'acqua secondo la normative europee

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Abstract

Directive 2000/60/EC and subsequent legislation provide a list of priority substances to be measured and monitored in EU water bodies and require the adoption of analytical methods that ensure comparability of the data collected in all Member States. These regulations and standards have gradually improved water quality in the EU. However, new drugs, whose effects on ecosystems and health are still to be determined, are detected with growing frequency. The Member States are now called upon to characterize and monitor these pollutants in view of their possible inclusion in the priority substance list

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Key words: water, monitoring, European directives, priority pollutants

Riassunto

La Direttiva 2000/60/CE e le successive normative in materia hanno individuato un elenco di sostanze prioritarie da misurare e monitorare nei bacini acquiferi dell'Unione europea, con l'adozione di metodologie che rendano i dati confrontabili in tutti gli Stati membri. Con l'introduzione di tali norme la qualità delle acque dell'UE ha subito un progressivo miglioramento, sebbene nuove sostanze, i cui effetti non sono stati al momento accertati, siano riscontrate frequentemente richiedendo l'impegno degli Stati membri per la caratterizzazione di tali inquinanti e per il loro monitoraggio al fine di inserirle a pieno titolo tra le sostanze prioritarie.

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Parole chiave: acqua, monitoraggio, direttive europee, inquinanti prioritari

INTRODUCTION

Surface waters receive large quantities of hazardous substances, which mainly derive from industrial, agricultural, domestic sources, and municipal sewage-treatment plants as well as surface runoff and atmospheric deposition. In this context, the Water Framework Directive (WFD; Directive 2000/60/EC) laid down criteria to protect inland surface waters, transitional waters, coastal waters and groundwater, to prevent their ecological decline, protect and enhance the status of aquatic ecosystems, promote sustainable water use based on long-term protection of available water resources, and contribute to mitigating the effects of floods and droughts. The Directive provides for the first time a list of substances, defined as priority pollutants (PPs), whose presence and levels need close monitoring, and lays down the methods to be applied to achieve compliance with legal PP levels to protect ecosystems and human health.

In addition to the PPs listed in Directive 2000/60/EC, public health bodies are also required to monitor a multitude of new substances, which over the past decade have been demonstrated to exert harmful effect on the environment and human health. At least two significant directives have amended Directive 2000/60/EC: Directive 2008/105/EC sets environmental quality standards (EQSs) for 30 PPs listed in Decision 2455/2001/EC and for eight other pollutants that were already regulated at EU level; and Directive 2009/90/EC sets technical specifications for chemical analysis and monitoring of water status, and minimum performance criteria for the analytical methods applied, which must be sufficiently sensitive to ensure that any overrun of EQSs is reliably detected and measured, with a view to providing understandable and relevant monitoring data.

The latest directive on water, 2013/39/EU, updated the list of PPs, which now total 45, redefines the criteria for assessing EQSs, and provides a watch list of substances whose mechanisms of damage to ecosystems and health are still unclear.

EQSs and threshold values for these substances need to be defined, to facilitate planning of priorities for action and to integrate data from the water analysis and monitoring programs implemented so far.

The new regulations reflect a change in focus with regard to the types of substances that are to be sought and monitored, and the main problems in water body management it seems to associate to what are known as emerging pollutants.

The water quality directives have led to the adoption by Member States of monitoring criteria and plans and of risk assessment methodologies for the substances included in the watch list. A key goal of the Water Framework Directive (WFD) and of the latest Directive is to achieve a good chemical status of waters. Comparing different directives with actual water quality, different approaches of standard settings are applied and potential treatment options are discussed. Each Member State has approved a National Implementation Plan (NIP) describing how each will meet the directive goals and the measures that will be implemented to eliminate or reduce the release of PPs into the environment by the use of best available techniques (BATs) and application of best environmental practices (BEPs).

The main innovation introduced by the latest directive is a watch list for 10 substances or substance groups, of specific matrices for their monitoring, and a list of methods of analysis that can be adopted, none of which entail excessive cost. The substances included in the watch list are selected from those that, according to available information, may present a significant risk for the aquatic environment and human health and for which monitoring data are currently insufficient. Diclofenac, 17-β-estradiol (E2), and 17-β-ethinylestradiol (EE2) are included in the first list and data are collected to facilitate the determination of measures to address the risks posed by these substances. The new mandate of the Working Group (2013 to 2015), approved by the Water Directors, envisages continuation of the activity on effect-based tools, in particular, in relation to the detection and evaluation of effects caused by mixtures of pollutants.

The aim of this paper is to gain insights into the problems associated with PPs and emerging pollutants at the European level, so as to improve the use of water quality indicators in the light of the new EU legislation.

METHODS

An overview of the literature published since 2000 and reports of international agencies regarding the concentrations of priority pollutants listed in the European directives on water safeguard by the official EU database, was made.

A PubMed search for papers addressing the levels of these chemicals in EU water bodies was conducted using «biomonitoring AND water», «priority pollutants AND water», «heavy metal AND water», «pesticides AND water», «organtin compounds AND water», «endocrine disruptor AND water» as the key words. Only papers with minimum performance criteria for the analytical methods applied were selected. A comparison of the ecological status of aquatic ecosystems with respect to the EQSs or maximum admissible concentrations (MACs) reported in the Directives for PPs, as well as the best monitoring action that better reflects the ecological risk associated with each class of discussed contaminant, was conducted.

RESULTS

Several methods have been applied to comply with the obligations set by the Directives and Member States have adopted the best technology and monitoring methods to measure PP levels in water basins and reduce them to meet legal targets. Pesticides have long been and still are an important class of contaminants in many EU countries. Their levels in several water samples collected from water mains, dug and deep wells exceeded MACs; in particular, simazine, fenitrothion, and diazinon MACs were exceeded in most samples, whereas those for DDT, methoxychlor, acephate, and atrazine were exceeded less frequently.[1]

A ranking index based on the measured concentrations of several priority pesticides in Spanish rivers and its ecotoxicological potential (EC50 values for algae, Daphnia sp., and fish), revealed a high risk for the aquatic ecosystems.[2] Notably, insecticides were identified as most important for Daphnia sp. (chlorpyriphos, chlorfenvinphos, diazinon, etc.) with RI up to 37%, followed by alkylphenols including octylphenol, nonylphenol, and related compounds. In Portugal, alachlor, atrazine, chlorfenvinphos, chlorpyrifos, endosulfan, simazine, and terbutryn detected in rivers exceeded their respective EQS values, with implications for the classification of the ecological status of surface water bodies in Portugal.[3]

Among all priority pesticides, agricultural insecticides constitute a major driver of animal biodiversity loss in freshwater ecosystems, and the global extent of their effects and the spatial extent of exposure remain largely unknown. Unfortunately, Europe – especially the southern and central European countries – represents a hotspot for insecticide contamination, as was pointed out by a predicted model for insecticides in global surface water developed by Ippolito et al.[4].

As regards to metals and metal compounds, cadmium (Cd), lead (Pb), and mercury (Hg) are included in the watch list. Metal contamination of water basins is declining, and although their concentrations are in the range set by the WFD for 2015, in some European water systems they may far exceed (up to 10-fold) the ground content limit set for 2021.[5] Nevertheless, monitoring programs only based on total metal determination in water have been recognized to be lacking, as metals present even at undetectable concentrations in water are strongly accumulated in fish. Moreover, when high concentrations of Hg are found in sediments, this indicates that the aquatic ecosystem may present pollution problems in regards to this metal, as demonstrated by the high Hg levels found in fish.[6-8] In order to evaluate the influence of metal pollution on the aquatic ecological status, several biological indicators, such as macroinvertebrates (IBMWP), diatoms (IPS), and macrophytes (IVAM), have been successfully considered from an integrated point of view.[8-11]

Recent data also show the advantage of a multidisciplinary approach based on bioindicator organisms and biomarkers of ex-

posure to monitor the acute and chronic adverse effects of both metals and organochloride compounds.[6,12,13]
Persistent organic pollutants (POPs) are a group of organic chemicals of special concern for their toxicity, persistence, long-range transport, and bioaccumulative potential. PCB levels often exceed the national EQS, such as data reported in the Venice lagoon (5-2,049 μg/kg and 4.24-239.15 μg/kg),[14] Oslofjord, Norway, (1-764 μg/kg),[15] the Sado River estuary, Portugal (1.3-114 μg/kg),[16] the Scheldt estuary, Netherlands–Belgium (0.47-136 μg/kg),[17] the Thau lagoon, France (2.53–33.32 μg/kg),[18] the intertidal zone of the North Sea (4.11-8.44 μg/kg),[19] the Guadiana estuary, Portugal (0.1-1.8 μg/kg),[16] and the Elbe estuary, Germany (2-85 μg/kg).[20] Data available range from heavily polluted to minimally impacted areas. In a wide monitoring study on global distribution of PCBs in the Mediterranean Sea, coastal lagoons reported PCB levels between 0.9 and 5,600 μg/kg.[21]
Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), despite their global distribution, have never been intentionally produced. However, a variety of chemical and thermal processes, including the manufacture of chlorinated intermediates and the combustion of chlorinated materials, can result in the formation and release of PCDD/Fs. There are some contaminated coastal areas in Europe, e.g., the Venice lagoon (16-126,561 ng/kg),[22] the Elbe estuary, Germany (711-169,605 ng/kg),[23] the Norwegian Grenlandsfjords (25,000-730,000 ng/kg),[24] and the Finnish Gulf (430-52,900 ng/kg),[25] while other areas show moderate contamination, e.g., the Thau lagoon, France (153-1656 ng/kg),[18] the Spanish northern Atlantic coast (0.15-3.99 ng/kg),[26] and the intertidal zone of the North Sea (0.124-3.156 ng/kg).[19]
Organotin compounds (OTCs) are widespread pollutants, frequently used as additives in antifouling agents for ships, which have contributed to the contamination of surface waters and aquatic systems in the last decades. These compounds exhibit a diversity of physical and chemical properties which offer various fields of application in industry and agriculture. In some European waters OTCs are found to be below the Directive's MAC.[27-29] Despite its decreasing contamination, TBT is still listed in the new directives, because of its persistent release from sediments, so much so that certain water bodies are still particularly contaminated with concentrations up to 110 ng/l.[30,31] Sampling of organotins in water is problematic, as normally large volume samples are needed in order to achieve the concentrations necessary to fulfil the current EQS requirements for TBT in the WFD (0.2 ng/l). Ultra-clean sampling containers and laboratories are necessary to achieve low background blanks, along with sensitive and robust instrumental methods. An alternative method for monitoring organotin compounds in water is the use of passive sampling, and this technique has received some attention over the past decade.
In a recent case study of representative Mediterranean rivers, more than 160 chemicals were detected in the Llobregat. Industrial compounds and pharmaceuticals were predominant, followed by personal care products, pesticides, perfluoroalkylated substances and illegal drugs.[32] A review on emerging contaminants in UK surface water and wastewaters reports approximately 70 pharmaceuticals belonging to a variety of therapeutic classes in UK environmental waters.[33] As regards pharmaceuticals, the latest water Directive (2013/39/EU) prescribes a number of actions for measuring them; once they have been characterized, Member States are required to begin their monitoring. Even though pharmaceutical products have been used for centuries, from an ecotoxicological viewpoint active pharmaceutical ingredients (APIs) are considered emerging environmental contaminants, because suitable and accurate analytical and sampling techniques to quantify them in environmental matrices have only recently been devised.[34] In this context, Petrie et al., (2015), highlight the importance of combined use of chemical analysis and biological indicators to better assess environmental impact from ECs, to avoid that transformation products go undetected and to develop a more accurate environmental risk assessment.

DISCUSSION

The present overview of studies, carried out to evaluate EU water policy objectives, which began to be set in 2000, documented only a small improvement in water quality in all Member States. Chemical status of a large proportion of water bodies is unknown due to poor chemical monitoring in many Member States, either because not all PPs are monitored or because few water bodies are monitored. A weak reduction in PP levels has been documented in water bodies across Europe, except those where PPs have been present longest. Nevertheless, organic substances with toxic properties such as pharmaceuticals, biocides, hormones, antibiotics, personal care products, flame retardants, and endocrine active substances, i.e., «emerging contaminants», are increasingly detected in the wider environment. Furthermore, the additive, synergistic, or antagonistic biological effects of those substances are not always clear because many of them are usually present at low or even barely detectable levels in surface waters, thus giving no clear evidence for their environmental risk.[35] This gap in knowledge has been covered by the use of both in vitro and in vivo bioassays[36,37] and by the use of biomarkers[6,13] for several kinds of contaminants.
Emerging contaminants are characterized by a diffuse presence in the environment, lack of knowledge of their medium- or long-term effects on human health and ecosystems, and poor coverage by current regulations. Among the mechanisms of action hypothesized for these contaminants, the most likely are endocrine disruptor chemicals (EDCs), adversely affecting development and reproduction. The classification criteria adopted for these substances, and for chemicals in general, include not only their environmental and health effects but also their production volumes.[38] The last World Health Organization (WHO) report, *State of the Science of Endocrine Disrupting Chemicals*, confirms that exposures to EDCs affect the reproductive health of wildlife species. Over the past 10 years, a high incidence and an increasing trend of many endocrine-related disorders in humans have been observed.[39] There has been a dramatic shift in focus from investigating associations between adult exposures to EDCs and disease outcomes to linking developmental exposures to disease outcomes later in life. Chil-

dren are the most vulnerable humans and exposure to EDCs during foetal development and puberty plays a role in the increased incidences of reproductive diseases, endocrine-related cancers, behavioural and learning problems, including ADHD, infections, asthma, and perhaps obesity and diabetes in humans.[39] In response to the potential hazard of EDCs in the aquatic environment, several screening programs have been implemented using a variety of chemical analyses. One of the main limitation is the possibility to detect their presence in water bodies at very low concentration levels (from µg/l up to pg/l), prioritizing the development of high-performance analytical techniques.[40] Analytical methods have been developed to successfully determine ultra-traces of target EDCs in the aquatic environment by gas chromatography coupled to mass spectrometry (GC-MS), or gas chromatography–tandem mass spectrometry (GC-MS-MS), as well as detecting estrogens in different matrices by liquid chromatography–tandem mass spectrometry (LC-MS-MS); recently, a new screening method has been introduced for EDCs employing stir bar sorptive extraction (SBSE). These methods provide the highest certainty of detection and the lowest detection limits, which are in the range of 0.1-0.5 for surface waters and in the range of 1-2 ng/l in sewage effluents. It has to be emphasized that effective concentrations are often in the range of the limit of detection.[41]
International literature, in accordance with the Water Directive guidelines, considers bioindicators as the best available means to meet their goals. These organisms are resistant to contamination and can accumulate pollutants, enabling the calculation of a relationship between concentration and the level of environmental alteration that has occurred over time. Bioindicators have the advantage of being easily available, practical to use even in special operating conditions (e.g., canals, drains, wells, etc.), robust, and inexpensive (most artificial supports such as DGT), enabling extensive testing.
To date, the adoption of different methods to detect PPs persists, depending on PP type and Member State. These discrepancies were the reason why Directive 90/2009/EC set criteria to ensure data consistency across studies.
Europe is a variegated area where river basin water management has undergone progressive homogenization in terms of both the methods used to measure PPs and water management. Directive 2009/90/EC laid down the criteria for EQS setting according to standard methods and processes across Europe. According to these criteria, high physicochemical water quality is one where synthetic pollutant concentrations are close to zero or below the limit of quantitation (LoQ) of the most advanced methods of analysis, and good if concentrations are lower than the EQSs.
In Italy, the reliability of the monitoring data provided by ARPA is ensured by the ISPRA Environmental Metrology Service through compliance with UNI EN ISO 17025 and uncertainty levels are close to the accepted limits. Data then undergo inter-comparison through collection of information on PP concentrations from various laboratories, to evaluate their overall quality. Directive 2013/39/EC requires member States to analyze the long-term trend of concentrations of PPs that tend to accumulate in sediment and/or biota, and define the frequency of monitoring. Member States may propose analyses to identify new PPs or priority hazardous substances, or to classify certain PPs as priority hazardous substances and, where appropriate, to set EQSs for surface water, sediment, or biota.

CONCLUSION

In conclusion, water pollution caused by wastewater effluents still persists, despite three decades of efforts to clean up European surface waters, the enforcement of anti-pollution laws, and increased monitoring of water bodies. Despite the successful reduction of the levels of some water pollutants, detection of emerging substances entailing public health risks indicates that the fight against water body pollution will have to take on ever newer threats. Even though it is difficult to eliminate the risk arising from exposure, it is possible to reduce its effects through synergistic action and the adoption of reliable detection methods.

Conflicts of interest: none declared

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