Emerging organic contaminants in aquatic environments: state-of-the-art and recent scientific contributions

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Resum. Els contaminants emergents són contaminants prèviament desconeguts o no reconeguts com a tals, la presència dels quals en el medi ambient no és necessàriament nova, però sí la preocupació pels possibles efectes perillosos sobre la salut humana i la dels ecosistemes. A causa de llur recent descobriment o reconeixement com a contaminants, la informació que se'n disposa sobre la presència, el destí i la toxicitat en ambients aquàtics, i sobre els mètodes analítics per a detectar-los en diverses matrius ambientals és escassa. En els darrers anys, el grup liderat pel professor d'investigació Damià Barceló Cullerès ha participat intensament en l'estudi de nombroses classes de contaminants emergents (estròg ens, fàrmacs, drogues, nanopartícules, plaguicides polars, etc.). Aquest article repassa les contribucions més recents fetes pel grup en aquest camp dels contaminants emergents en les línies de desenvolupament de mètodes analítics, programes de vigilància ambiental i estudis de biodisponibilitat, degradació i toxicitat.

Paraules clau: contaminants emergents · anàlisi d'aigua · monitoratge ambiental · biodisponibilitat · productes de degradació · toxicitat

Summary. Emerging contaminants are previously unknown or unrecognized contaminants whose presence in the environment is not necessarily new but which raise concern due to their potentially dangerous effects on the ecosystem and on human health. Due to their recent discovery or recognition as contaminants, information about the occurrence, fate, and toxicity of these compounds in the aquatic environment, as well as analytical methods for their detection in various environmental matrices, is scarce. We have intensively studied many of these classes of emerging contaminants (estrogens, pharmaceuticals, illicit drugs, nanoparticles, polar pesticides, etc.). This article reviews the most recent contributions made by our group to the field of emerging contaminants with respect to the development of analytical methods, monitoring studies, and bioavailability, degradation, and toxicity studies.

Keywords: emerging contaminants · water analysis · environmental monitoring · bioavailability · degradation products · toxicity

Introduction

In the past, most of the worldwide environmental research focused on the study of the presence and toxicity of so-called persistent organic pollutants (POPs), which include toxic and bioaccumulative compounds, such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and dioxins. Many of these chemicals were thus recognized as priority pollutants and therefore subjected to regulation. However, over the last few decades, the development of new and more sensitive analytical techniques has evidenced the presence of a much larger number of potentially dangerous compounds, globally known as emerging contaminants. These are defined as previously unknown or unrecognized contaminants and they are suspected of posing a real or perceived threat to human health or the environment; however, either there are no currently published health standards, or the scientific basis of current standards is evolving or being reevaluated.

Due to their recent discovery or recognition as contaminants, there is little information about the occurrence, fate, and toxicity of these compounds in the aquatic environment, nor are there analytical methods for their determination in the various environmental compartments. In addition, most emerging contaminants are produced and consumed in high amounts and, as a consequence, their introduction in the aquatic environment is continuous. Therefore, since they do not need to be persistent to cause negative effects they are considered pseudo-persistent contaminants.

The list of emerging contaminants includes a wide variety of compounds used daily in industrial as well as household applications. Some of them, after intensive investigation and the generation of sufficient evidence of the danger they pose, have been included in the list of priority substances in the field of water. This is the case of polybrominated diphenyl ethers (PB-

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DEs), used mainly as flame retardants; the degradation products of alkylphenol ethoxylate (APEO) surfactants, octylphenol (OP) and nonylphenol (NP); and chlorinated paraffins. Other compounds, such as pesticides, have been regulated in water for many years, but the discovery of toxic degradation products has led to renewed interest in them. Finally, for most emerging contaminants, such as pharmaceuticals, perfluorinated compounds, and nanoparticles, the currently available information is insufficient to allow proper evaluation of their risk and hence the adoption of potential measures to prevent or diminish exposure to them. In addition, some of these emerging contaminants, e.g., PBDEs, APEOs, and certain pharmaceuticals, are endocrine disruptors, i.e., compounds that interfere in the normal functioning of the endocrine system and alter the normal growth, development, reproduction, and behavior of organisms. One of the best documented endocrine-disrupting effects is the feminization of fish following exposure to estrogenic compounds.

During the last several years, the research group headed by Professor Damià Barceló has been intensively involved in the study of many of these classes of emerging contaminants (APEOs, estrogens, PBDEs, pharmaceuticals, polar pesticides, etc.). The group's five main lines of research have been: (i) the development of analytical methods, (ii) environmental studies, (iii) bioavailability studies, (iv) degradation studies, and (v) toxicity studies.

Development of analytical methodologies for detection of emerging contaminants

The first step to advance knowledge of emerging contaminants is to develop analytical methods for their detection in the various aquatic environmental matrices, including surface waters, groundwater, wastewater, drinking water, and in those related to them, such as sediments and soils. These methods can then be further applied in environmental studies to assess the occurrence of emerging contaminants and in the identification of the most problematic compounds and areas, which may allow the implementation of actions aimed at improving water quality, reducing exposure, and/or optimizing the use of available water resources.

For a meaningful assessment of the chemical and ecological status of the aquatic environment, these activities have to be complemented with bioavailability studies to determine the fraction of pollutants that is truly accessible to organisms, with degradation studies to identify degradation products that may also be harmful to the aquatic environment, and with toxicity studies for effective risk assessment.

Due to the recent discovery of emerging pollutants (and/or their effects), methods for their environmental analysis are few or simply do not exist. In the last two years, our group has contributed to this field with the development of new methods to analyze the flame retardant hexabromo-cyclododecane in sediment samples [13]; beta-blockers in wastewaters (using molecular imprinted polymers for extraction) [12]; drugs of abuse in sewage water [25] and in airborne particles [28]; polar pharmaceuticals in wastewaters [2], environmental waters [11], environmental solid samples [14], and sludge [32]; and phytoestrogens, progestogens, and estrogens in environmental waters [19].

These methodologies rely on the use of the most advanced extraction techniques: fully automated on-line solid phase extraction (SPE) for liquid samples and pressurized liquid extraction (PLE) for solid samples; purification techniques (based on SPE with conventional sorbents, such as silica or polymeric sorbents, or newly developed materials, such as molecularly imprinted polymers and restricted access materials), and analytic techniques. The latter include conventional liquid chromatography (LC) and ultra performance liquid chromatography (UPLC), both coupled to tandem mass spectrometry (MS/MS) with different ionization interfaces (electrospray and atmospheric pressure chemical ionization) and analyzers, such as triple quadrupole (QqQ), quadrupole-linear ion trap (QqLIT), and quadrupole-time of flight (QqToF).

With respect to environmental studies, they mostly have been performed in areas of particular interest, i.e., where water is scarce or of poor quality. In this line of research, the occurrence of polar pesticides [20,22,27], flame retardants [5], pharmaceuticals [15,20,29,30], illicit drugs [25,26,28], estrogens [20], surfactants [10], and other classes of emerging contaminants has been studied in different types of matrices (waste, natural and treated waters, river sediment, fish, sludge, etc.) from very diverse areas: the river basins of the Ebro [6,15], Llobregat [20], Besós [30], and Guadiana, and other areas outside Spain, such as Portugal [22] and Brazil [19].

Monitoring, bioavailability, degradation, and toxicity studies

Results obtained in these studies have often been publicized in the media. This was the case in our study of illicit drugs in various Spanish wastewater treatment plants (WWTPs), with consumption of the different drugs (cocaine, cannabis, heroin, ecstasy, etc.) by residents of the investigated cities estimated [26]. Other examples are the detection of some illicit drugs in the air of Madrid and Barcelona [28], the detection of carbon nanoparticles in effluent wastewater suspended material from 22 WWTPs in Catalonia [9], or the finding of many pharmaceuticals at high concentrations in river waters [11]. Intense focus has been placed also on investigations of the removal efficiency of water treatment processes, both conventional and modern (nanofiltration), and of membrane bioreactors [10,15,20,29]. We have also investigated groundwater since most of the drinking water in Spain comes from rivers and swamps and many of these sources are insufficient to meet social and economic demands throughout the year. The exploitation of aquifers is highly variable and, if in some areas the phreatic level is critical due to overexploitation and the construction of illegal wells, in others it is so high that it ends up causing floods in urban areas (garages, first floors, etc.). This was recently the case in Barcelona. In addition, groundwaters have always been considered to be of good quality due to natural attenuation. However, recent studies demonstrated that the groundwater

quality is progressively worsening. Thus, various projects have been initiated to assess the chemical quality of groundwater, both to test whether there is compliance with EU legislation and to explore alternative exploitation, such as using poor-quality groundwater for garden watering [27,30,34].

Bioavailability studies are required to properly evaluate the ecological impact of pollutants. Studies of this type have been conducted both in water (with passive samplers) and in solid environmental samples (with Tenax). Gentle extraction with Tenax has been used to investigate the kinetics of desorption of different PBDEs from sediments [3], whereas passive samplers have been evaluated for the time-integrated sampling and analysis of PBDEs [4] and estrogens [18] in water.

Another aspect that raises increasing concern is the awareness that many pollutants, priority or emerging, are metabolized or undergo transformation in the environment. The formation of degradation products (DPs) takes place principally under two conditions: during wastewater treatment and in the aquatic environment itself, with biodegradation and photodegradation being the most common processes. In many cases, the generated substances may be more potent and more noxious than the parent compounds and the immense majority of them are still unknown. Experiments of this type have been carried out under controlled laboratory conditions (redox, temperature, etc.) and in some cases they have been completed with field tests. The focus has been primarily on pharmaceuticals due to their probable capacity to exert adverse effects on the environment. In this context, tests that include the identification and structural characterization of biodegradation products of the beta-blocker atenolol and the anti-diabetic glibenclamide [31], of phototransformation products of the X-ray contrast medium iopromide [23], and of metabolites of the analgesic diclofenac and the lipid regulator clofibric acid [17] have been carried out. The formation of various disinfection by-products of triazine pesticides in drinking water (after chlorination) has also been investigated [1]. The most important techniques used for the identification of metabolites and degradation products have been UPLC-QqTOF-MS/MS, and LC-QqLIT-MS/MS.

Finally, the assessment of water quality requires the use of both chemical and biological methodologies not only to detect contaminants but also to identify possible undesired effects in the environment. For evaluation of these effects, different toxicity assays have been applied in combination with chemical analysis. In the delta of the Ebro River, for instance, the analysis of pesticides in water and seafood has been combined with ecotoxicity measurements of the water using three different organisms (the micro-crustacean *Daphnia magna*, the alga *Pseudokirchneriella subcapitata*, and the bioluminescent bacteria *Vibrio fischeri*). Based on the results, it was concluded that pesticides most probably play a positive role in the mortality of oysters and mussels periodically observed in this area [16]. A similar integrated approach, performed in this case in the Llobregat River, pointed out a potential causal association between the concentrations in river water of some anti-inflammatories and beta-blocker pharmaceuticals and the abundance and biomass of several benthic invertebrates (*Chironomus* spp. and *Tubifex tubifex*) [21]. Some years ago, a similar approximation allowed our group to provide evidence, for the first time in Spain, of the existence of intersex fish (specimens with both male and female reproductive organs) in Spanish rivers and the relationship between this phenomenon and exposure to estrogenic compounds present in the river's waters and sediments [24,33]. Finally, other studies have investigated the ecotoxicological impact of nanomaterials, which are among the most recently identified emerging contaminants [7], PBDEs [5], pharmaceuticals [8], dioxin-like compounds [6], etc.

The methodologies/results described in these studies have often been the first of their type published in the scientific literature, demonstrating the limited information available. Many of these studies have been possible thanks to the collaboration of water agencies such as the Catalan Water Agency (ACA), the Barcelona Water Services Group AGBAR, and the Hydrographic Confederation of the Ebro (CHE). The ultimate objective has been to fill knowledge gaps regarding the presence and fate of emerging contaminants in aquatic environments and to help protect humans and the environment against the potentially dangerous consequences of exposure to these compounds, in an effort, at the same time, to improve the quality and sustainability of water resources.

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Damià Barceló completed his Ph.D. in Analytical Chemistry (1984) at the University of Barcelona. Since 1999, he has been full Research Professor at IDAEA-CSIC, in Barcelona. At present, he is Deputy Director of the IDAEA-CSIC, Director of the Catalan Institute for Water Research (ICRA), in Girona, and Visiting Professor at King Saud University, Riyadh, Saudi Arabia. He was awarded the 2007 King James I Prize on the Protection of Nature. He has published close to 600 scientific papers in SCI journals (Hirsch-Index 64) and 100 book chapters, and is editor of 8 books on environmental analysis and co-author of one book on pesticides. Other relevant activities are: networking experience at the EU (1997–2002) and coordination of the Waste Water Cluster (2002–2004) and various other EU projects related to water and soil quality. He has supervised 31 Ph.D. theses on environmental analysis. His scientific focus is on method development and the monitoring of priority, new, and emerging pollutants, including endocrine-disrupting compounds, using advanced mass spectrometric analysis, such as LC-MS/MS, and hybrid instruments, such as LC-QqTOF-MS/MS and LC-QqLIT-MS/MS, combined with bioassays and endocrine effect studies.