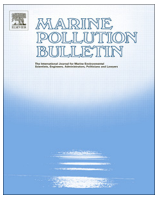
Marine Pollution Bulletin xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul



Sources, fluxes and risk of organic micropollutants to the Cantabrian Sea (Spain)

Juan Sánchez-Avila [a], Joana Vicente [a], Beatriz Echavarri-Erasun [b], Cinta Porte [a], Romà Tauler [a], Silvia Lacorte [a,*]

[a] Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain
[b] Institute of Environmental Hydraulics (IH Cantabria), University of Cantabria c/ Isabel Torres 15 (PCTCAN), 39006 Santander, Spain

ARTICLE INFO

Keywords:
Organic micropollutants
Coastal and estuarine seawater
Sediments and mussels
Pollution sources
COMMPS procedure
Site risk indexes

ABSTRACT

The sources, distribution and risk of 51 organic micropollutants (OMPs) in the Cantabrian coastal environment (NW Spain) were evaluated. Gas chromatography coupled to tandem mass spectrometry was used to determine polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorinated pesticides, polybrominated diphenyl ethers, phthalates esters, bisphenol A and alkylphenols. 45 OMPs were detected in coastal/estuarine waters. Wastewater treatment plant effluents and emissary discharges were identified as the main sources of contamination. The accumulation of OMPs in sediments and the bioaccumulation in 21 days caged mussels were also assessed. Chemical results were combined with the "Combined Monitoring-based and Modeling-based Priority Setting Scheme" COMMPS procedure for risk assessment analysis. Finally, the chemical status of the different sampling locations was estimated using site risk indexes. Those indexes can be conveniently displayed in quality geographical maps and are considered a valuable tool for the environmental management and risk assessment of the region under study.

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1. Introduction

Industrial, municipal and treated or untreated wastewater discharges through smokestack, pipe, ditch, tunnel, or conduit are identified as point source pollution to coastal areas (European Environment Agency, 1995). Point source pollution can contribute in the form of oxygen-depleting nutrients and pathogens that cause serious health hazards to the environment (Xiao et al., 2012). In addition, these point sources can significantly contribute to coastal water pollution in the form of toxic organic contaminants (Sanchez-Avila et al., 2009) and heavy metals (De los Ríos et al., 2012). The magnitude of the pressure (industry, population, agricultural run-off) and vulnerability of receiving water (geographic, climatic and hydrology, dilution capacity, protection of the area, existing monitoring surveys) are the main factors that explain the impact of the discharges. Other activities such as shipping, motor boats and port activities (Mestres et al., 2010), oil spillages (Soriano et al., 2007), ballast water discharges and litter (European Environment Agency, 1995) also affect the quality of coastal waters.

The Cantabrian Sea is located in the Northern Spain, comprising the Autonomous Communities of Asturias, Cantabria and The Basque Country. This region is characterized by a mild weather, strongly influenced by oceanic water affluence from the Atlantic Ocean and the West winds circulation accompanied by low pressure systems (European Environment Agency, 2002). Approximately 1.25 million persons inhabit in this coastal municipalities (Spanish National Institute of Statistics, 2006). This coastal area is highly industrialized with textiles, food, chemical, petro-chemical, mining, automotive industry, metals transformation, waste management facilities, ports and dredging activities (Basque Country Water Agency, 2006). This region was revealed as a contaminated by perfluorinated compounds (Gómez et al., 2011) and by phthalate esters (PEs), bisphenol A (BPA), alkylphenols (APs) and metals (De los Ríos et al., 2012) in water, sediments and mussels; polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), PEs, butyltins, and metals in mussels (Bartolomé et al., 2010); and PAHs in mussels (Soriano et al., 2007), sediment and fish (Puy-Azurmendi et al., 2010).

Current strategies to monitor the impact of organic micro-pollutants (OMPs) in coastal systems should combine the monitoring of water–sediment–biota compartments to provide comprehensive information on the presence and fate of OMPs. OMPs are adsorbed to particulate matter and are easily sedimented, and sediments become a reservoir of contaminants (Rudolf, 1991). On the other hand, OMPs in the water column or resuspended from sediments can be accumulated by organisms (Baumard et al., 1998). Among others, mussels (*Mytilus* sp.) have been widely used as bioindicators of contamination (Baumard et al., 1999; Valavan-

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* Corresponding author. Tel.: +34 934006133; fax: +34 932045904.
E-mail address: slbqam@idaea.csic.es (S. Lacorte).

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http://dx.doi.org/10.1016/j.marpolbul.2013.04.010

Please cite this article in press as: Sánchez-Avila, J., et al. Sources, fluxes and risk of organic micropollutants to the Cantabrian Sea (Spain). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2013.04.010

idis et al., 2008). They have a wide distribution, abundance; have a sedentary behavior, and a pronounced ability to accumulate organic compounds. Filter-feeding mussels process large volumes of sea water (approximately 2 dm^3 per hour), thereby accumulating organic compounds in concentrations two to five orders of magnitude greater than those in the ambient seawater (Goldberg, 1986). The pattern of organic pollutant concentrations detected in mussels could therefore resemble their pattern in the ambient water to a good approximation (Potrykus et al., 2003). Recently, the European Commision (2011) proposed to include monitoring of biota such as mussels, within the environmental quality standards (EQSs) established by the Directive 2008/105/EC (European Parliament and Council, 2008).

The objective of the present study was to evaluate the sources of OMPs (such as WWTP effluents, submarine emissaries and industrial discharges) to estuarine and coastal waters from the Cantabrian Sea and to assess the risk, considering the concentration of OMPs, their specific toxicity, the frequency of detection and the fluxes released towards coastal areas. Chemical analyses combined with risk assessment were used to discern the impact of OMPs to coastal areas.

2. Materials and methods

2.1. Study area and sample collection

Waters, sediments and transplanted mussels were sampled in estuarine and coastal areas from Asturias, Cantabria and Basque Country (North Spain). These areas receive mainly the discharges of treated or untreated urban wastewaters via emissaries, run-off of industrial wastes and port activities. Table 1 describes the matrices sampled in each site, their coordinates and the principal pressures/impacts affecting each site. Sites were grouped in three categories according the principal pressures:

(a) 2 Coastal waters with WWTP discharges through submarine emissaries (VM, PÑ), 1 coastal water with no identified pressures/impacts (BE) and 3 estuarine waters with uncontrolled discharges (SV, UR, PL)
(b) 3 Estuarine waters with port/harbor activities (PA, PP and PS) or in the proximity of industrial (FE) and WWTP effluents (GA).
(c) An additionally group included 2 WWTP effluents (WG, WS).

The submarine emissaries VM and PÑ were sampled at three depths: at the outflow of the emissary, at the bottom of the sea (30 m deep); at 15 m deep and at 1 m deep from the surface. Besides, in order to compare the pollution levels with a reference site, a distant control site with similar geomorphologic features was selected (BE). BE was sampled in the same way as VM and PÑ. The rest of the estuarine waters were collected at 1 m deep. All the sediments were taken at the sea bed. All samples were collected in 1 L clean amber glass bottles. To avoid sample manipulation and prevent any cause of external contamination during sampling and extraction, samples were transported, stored and analyzed in the same bottle used for sampling. After collection, samples were stored at 4 °C until transport to the main laboratory and waters were processed within 1 week while sediments were frozen, freeze dried and sieved through 120 μm. In PP, sediment was not sampled because the seabed was covered with rubble and scrap iron (see Table 1).

Transplanted mussels were placed in the above mentioned sites for a period of 3 weeks. First, 40–50 mm length mussels were collected from mussel crops from the Galician Rías (NW Spain), cleaned from epiphytes and caged in polyethylene experimental units. Experimental units were acclimated in an open circuit aquarium for 7 days. Before placing the mussels in each study site, 10 individuals from four experimental units were collected to quantify the contamination levels before the exposure (t_0). The experimental units were anchored onto fixed structures at 30 m depth (BE, VM and PÑ) while in the other stations were held between 1 and 4 m of depth. After 21 days of exposure (t_{21}), 10 additional mussels were collected, except from PÑ where the experimental unit was lost because of a storm. Once collected, 10 mussels were ground to a homogenized mix, freeze dried, homogenized again and kept in a glass jar at −20 °C until extraction.

Sampling was carried out in October 2009 (t_0) and repeated in November 2009 (t_{21}). Sampling was performed by professional scuba-divers.

2.2. Analytical procedure

Fifty-one target compounds, summarized in Table 2, were analyzed in water, sediment and mussels samples as detailed in Sánchez-Avila et al. (2011). Briefly, unfiltered water samples (1000 mL of coastal/estuarine/surface waters or 250 mL of WWTP effluent) were spiked with the surrogate standards (acenaphthylene d_8, benzo(a)pyrene d_{12}, benzo(g,h,i)perylene d_{12}, fluoranthene d_{10}, phenanthrene d_{10}, pyrene d_{10} PCB 209, 4-n-nonylphenol-d_8 and bisphenol A-d_{16}) at 10 ng L^{-1} in seawaters and at 100 ng L^{-1} in WWTP effluents and were solid phase extracted using Oasis HLB 200 mg cartridges. Extracts were reconstituted with 100 μL of ethyl acetate and spiked with 0.1 ng μL^{-1} of the internal standard anthracene d_{10}.

One gram of homogenized mussels (*Mytilus galloprovincialis*) or homogenized sediments (<120 μm fraction) were spiked with the surrogate standards at 200 ng g^{-1}. Samples were liquid–solid ultrasound-assisted extracted (10 min) using 1 × 10 mL of dichloromethane/hexane and 2 × 10 mL of hexane/acetone (in triplicate). After extraction, samples were centrifuged for 10 min at 2500 rpm. Extracts were combined and concentrated to approximately 1 mL under a nitrogen current using a TurboVap LV at 25 °C. Extracts were subsequently purified using Florisil (5 g) SPE cartridges (Waters, MA, USA), previously conditioned with 20 mL of hexane/dichloromethane (1:1 v/v) and 20 mL of hexane/acetone (1:1 v/v). The sample extract was eluted with 15 mL of hexane/dichloromethane (1:1 v/v) and 15 mL of hexane/acetone (1:1 v/v). The eluent was evaporated until almost dryness under a nitrogen current at room temperature and reconstituted with ethyl acetate to a final volume of 200 μL for mussels and 500 μL for sediments. Internal standard anthracene d_{10} was added at a concentration of 1 ng μL^{-1}.

Extracts were analyzed using an Agilent 7890A GC System (Agilent Technologies, Palo Alto, CA, USA) interfaced to a 7000A triple quadrupole mass spectrometer system (Agilent, USA) in electron ionization mode (EI, +70 eV). Two μL of each extract were injected using an Agilent 7683A autosampler, following the conditions optimized previously by Sánchez-Avila et al. (2011). The use of two transitions (one precursor with two product ions or two precursors with one product ion) confirms positive findings by Selected Reaction Monitoring (SRM) according to European legislation (European Commision, 2002). Quantification was performed using the internal standard method. A nine points calibration curve was analyzed in duplicate from 0.010 to 1.0 ng μL^{-1} for all target compounds except for the PBDEs (0.010 to 0.10 ng μL^{-1}). Good linearity responses were obtained over the concentrations range tested for all target pollutants. The coefficients of determination (R^2) obtained were higher than 0.991. The methodological detection limits (MDLs) and recovery yields are described in Sánchez-Avila et al. (2011).

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