Organic micropollutants in coastal waters from NW Mediterranean Sea: Sources distribution and potential risk

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ABSTRACT

This study provides a first estimation on the sources, distribution and risk of organic micropollutants (OMPs) in coastal waters from NW Mediterranean Sea. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorinated pesticides, polybrominated diphenyl ethers, phthalates and alkylphenols were analyzed by solid phase extraction and gas chromatography coupled to tandem mass spectrometry (SPE–GC–EI-MS/MS). River waters and wastewater treatment plant effluents discharging to the sea were identified as the main sources of OMPs to coastal waters, with an estimated input amount of around of 25,800 g d^{-1}. The concentration of ΣOMPs in coastal areas ranged from 17.4 to 8442 ng L^{-1}, and was the highest in port waters, followed by coastal and river mouth seawaters. A summarized overview of the patterns and sources of OMP contamination on the investigated coastal sea waters of NW Mediterranean Sea, as well as of their geographical distribution was obtained by Principal Component Analysis of the complete data set after its adequate pretreatment. Alkylphenols, bisphenol A and phthalates were the main contributors to ΣOMPs and produced an estimated significant pollution risk for fish, algae and the sensitive mysid shrimp organisms in seawater samples. The combination of GC-MS/MS, chemometrics and risk analysis is proven to be useful for a better control and management of OMP discharges.

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1. Introduction

Chemical pollution in marine waters presents a threat to the aquatic environment with effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as threats to human health (2008). However, the impact of organic micropollutants (OMPs), such as phthalate esters, pesticides and other endocrine-disrupting compounds in the marine environment is poorly studied (Gimeno et al., 2004). Among those, coastal waters have become vulnerable areas because of their intermediate position between open seas and human activities (Nellemann and Corcoran, 2006; Sánchez-Avila et al., 2010a). The increase in population and industrial pressure along rivers and coastal areas poses an important threat on those coastal ecosystems since OMPs are accumulated in sediments and biota and become a source to other organisms. A wide variety of OMPs are present in coastal and marine ecosystems, including polycyclic aromatic hydrocarbons (PAHs) (Valavanidis et al., 2008), plasticizers such as phthalate esters (PEs) and bisphenol A (BPA) (Fromme et al., 2002), organochlorine pesticides (OCPs), alkylphenols (APs) (Sánchez-Avila et al., 2010b), polychlorinated

biphenyls (PCBs), and polybromodiphenyl ethers (PBDEs) (Pérez-Carrera et al., 2007), among others. OMPs are daily discharged to seawater principally via wastewater treatment plant effluents (WWTP) and also river inputs which can transport pollutants from inland activities (Céspedes et al., 2006; Gómez-Gutiérrez et al., 2007a; Sánchez-Avila et al., 2009).

The low concentrations of micropollutants in the marine environment in addition to the complexity of those matrices are two major difficulties associated with the detection and quantification of OMPs. The progress on the development of new and more powerful analytical methods has made available their determination in rivers, seawater and wastewater at concentrations of ng L^{-1} (Sánchez-Avila et al., 2011). In addition, multiresidue methods permit the analysis of a wide range of pollutants with varying physicochemical parameters in a single run which in terms of cost and time, in front of family-related compound using different methodologies, is beneficial because they can "capture" all the chemical information of a sample (Lacorte et al., 2000). However, routine monitoring and reporting of abiotic and biotic concentrations of OMP are of limited use, unless such data can be related directly to the assessment of public health and ecological risk (Wu et al., 2008). Ecological risk assessment can be estimated under diverse methodologies, such as the combined monitoring-based and modeling-based priority setting (COMMPS) procedure, which is applicable when there exists a large monitoring database (Teixido et al., 2010). The tool used herein for assessing the ecological risk involves a comparison between

environmental concentrations (either predicted, PEC, or measured, MEC) with predicted no effect concentrations (PNEC), denominated Risk Quotients (RQs) (Sanderson et al., 2004; Wu et al., 2008). PEC values are calculated using several models taking into consideration application rates, persistence, leaching, sorption and compound bio-accumulation or directly from monitoring data while PNEC values are usually calculated on the basis of critical concentrations, e.g. EC_{50}, LC_{50} (50% effect concentration or 50% lethal concentration, respectively) and NOEC (non-observed effect concentration). Monitoring data must be compared with toxicological data and concentrations of contaminants below adverse effects thresholds are of little environmental concern (except, perhaps, for identifying the source of contamination).

The Catalan Coast is a highly urbanized region of the NW Mediterranean Sea with important industrial and agricultural activities. Coastal waters receive the continuous input from treated and untreated WWTP discharges, run-off and river waters. This coastal zone has been studied previously and several OMPs have been detected, suggesting that anthropogenic activities have an impact on coastal water quality, sediments and biota. For example, DDT and PCBs (Bayona et al., 1991; Gómez-Gutiérrez et al., 2007b; Scarpato et al., 2010) and PAHs (Baumard et al., 1999; Galgani et al., 2011) were identified in sediments, mussels and also in fish tissues (Albaiges et al., 1987). Those findings reveal the Catalan coast area as "hot spot" area for pollutants. However very few data has been reported on the OMP concentration in the seawater and the risk this may pose to the coastal ecosystem.

The objective of the present study was to evaluate the occurrence and mass flow of 51 target OMPs (PAHs, PEs, BPA, APs, OCPs, PCBs and PBDEs) to the NW Mediterranean sea (Catalan coast), considering rivers and WWTP effluents discharging to the sea as pollution sources and seawater as receptor. The inputs of OMPs in coastal waters were estimated according to the levels of target pollutants detected in river waters and WWTP effluents discharging to the sea via submarine emissaries and their specific fluxes. Principal Component Analysis (PCA) was applied to the experimental data set in order to identify main sources of OMP contamination and their distribution. Finally, RQs were estimated using fish, algae and mysid shrimp as reference organisms to assess the environmental risk of OMPs in the NW Mediterranean coastal waters.

2. Materials and methods

2.1. Study area and sample collection

The study area comprised the NW Mediterranean Sea (Table 1), from Roses in Catalonia, Spain (42.1544° N, 3.1807° E) to Castellón in Valencia, Spain (39.9697° N, 0.0140° E). Table 1 reports the details about the sample locations, the type of waters sampled, the co-ordinates and the characteristics of each site. Sampling was carried out in spring–summer 2009 (from March to July). Forty six seawaters were sampled which corresponded to 22 coastal waters (C1 to C22), 7 seawaters collected at the mouth of a river (M01 to M07) and 17 ports (P1 to P17). These sampling locations comprised all municipalities with more than 5000 inhabitants and some had important industrial activities (Table 1). In addition, all WWTP (W1 to W8) treated effluents discharging in this coastline via submarine sea emissaries were analyzed. Finally, the main 6 rivers (R1 to R6) discharging to the NW Mediterranean were sampled. It is important to remark that rivers were sampled in low flow conditions which represent the "worst case scenario". Originally the sampling covered more Catalan rivers which could not be sampled because they were dry in this period. All water samples were collected in 1 L clean

amber glass bottles previously washed with water and Extran (Merck, Darmstadt, Germany), rinsed with distilled water and acetone and baked at 450 °C to eliminate organic matter. To avoid sample manipulation and prevent any cause of external contamination during sampling and extraction, waters were transported, stored and analyzed in the same bottle used for sampling. Transport and storage were done maintaining samples at 4 °C. All samples were extracted within 48 h of collection to avoid degradation of target compounds. For river and port water collection, bottles were placed in a drag for a better accessibility to the samples. Grab seawater (coastal and river mouths) samples were collected by an expert swimmer at 50 to 100 m from the coast line and at 1 to 2 m deep. Port seawater grab-samples were collected near the port mouth at 1 to 2 m deep. River grab-samples were collected in the middle of the river flow at 1 m depth at the mouth of the river (3-10 km inland). The WWTP samples were made of 24 h composite aliquots taken from the effluent.

2.2. Extraction and gas chromatography coupled to mass spectrometry analysis

The analytical procedure was based on a previously reported validated method based on solid phase extraction Oasis 200 mg cartridges and gas chromatography coupled to tandem mass spectrometry for the determination of 51 OMPs (16 PAHs, 4 APs, BPA, 5 PEs, 7 PCBs, 6 PBDEs, 12 OCPs (including isomers or degradation products) in sea, river waters and WWTP effluents (Sánchez-Avila et al., 2011). The optimized conditions permitted to determine ultra low ng L^{-1} level concentration of the OMPs in the different water matrices studied.

Unfiltered water samples (1000 mL of sea or river waters or 250 mL of WWTP effluent) were analyzed to avoid sub-estimations in the total concentration and thus, both dissolved and particulate bound chemicals were considered. 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}) were added prior to preconcentration at 10 ng L^{-1} in sea or river waters and at 100 ng L^{-1} in WWTP effluents. After extraction, samples 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 EI (+70 eV). Two μL of each extract was injected using an Agilent 7683A autosampler. 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 the European legislation (Commission of the European Communities, 2002). Quantification was performed using the internal standard method. A 9 point calibration curve was analyzed in duplicate from 0.010 to 1.0 ng μL^{-1} for all target compounds except for PBDEs (0.010 to 0.10 ng μL^{-1}). Good linearity responses were obtained over the concentration range tested for all target pollutants. The coefficients of determination (R^2) obtained were higher than 0.9910. The methodological detection limits (MDL) and recovery yields are described in Sánchez-Avila et al. (2011).

2.3. Statistical analysis

Statistical significance of results was determined by the one-way analysis of variance (one-way ANOVA).

2.4. Principal Component Analysis

To establish relationships between sources and seawater pollution, a multivariate exploratory data analysis study was performed using Principal Component Analysis (PCA) (Jolliffe, 2002). PCA is a