# Distribution and fate of legacy and emerging contaminants along the Adriatic Sea: a comparative study

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## Abstract

The spatial distributions and fates of selected legacy and emerging compounds were investigated and compared in surface sediments sampled along the Adriatic mud-wedge and in deep-sea regions from the southern Adriatic basin. Results indicated that the concentrations of legacy contaminants (PAHs, PCBs and DDTs) and emerging contaminants (tonalide, galaxolide, EHMC, octocrylene, BP3 and NP) ranged from 0.1 to 572 ng $g^{-1}$ and from <LOD to 40.7 ng $g^{-1}$, respectively. In general, higher concentrations and estimated burdens were detected in the northern Adriatic, highlighting the importance of the Po River as the major contributor for the inputs of legacy and emerging contaminants to sediments in the Adriatic Sea. Nevertheless, the prevalence of some UV filters and fragrances in the central and southern Adriatic indicates that the proximity to tourist areas and WWTPs discharges seems to affect the distribution of those compounds. The accumulation of contaminants in the deep-sea areas supports the inference that this region may act as an important repository for contaminants within the Adriatic Sea. Estimated annual contaminant accumulation reveals that both, legacy and emerging contaminants accumulate preferentially in the northern Adriatic (40 to 60% of the total annual contaminant accumulation), where the presence of legacy, and to a lesser extent emerging contaminants, are likely to pose an immediate or long-term hazard to resident biota.

**Keywords:** emerging contaminants, Adriatic mud-wedge, hazard quotients, total mass, contaminant accumulation

## Capsule

Legacy and emerging contaminants accumulate preferentially in the northern Adriatic. Large-scale circulation transfers sediment-bound contaminants to deep-sea regions in the southern Adriatic.

## Introduction

There are currently more than 85,000 chemicals in production and use world-wide, a fraction of which is accumulated in marine and coastal areas through deliberate dumping, natural runoff from the land or atmospheric deposition (Sahu et al., 2009; McKnight et al., 2015). Therefore, there is a growing concern over the last decades about the environmental distribution and the potential effects of these synthetic substances. Environmental policies and efforts are being made at different levels in order to achieve a comprehensive understanding and protection of marine systems. For instance, the Marine Strategy Framework Directive (MSFD) has been adopted at European level in order to achieve Good Environmental Status (GES) of the EU's marine waters by 2020, addressing data availability, knowledge gaps and research priorities regarding contaminants and marine pollution impacts (2008/56/EC; European Commission, 2008).

Persistent organic pollutants (POPs; e.g. polychlorinated biphenyls - PCBs, polycyclic aromatic hydrocarbons – PAHs, and chlorinated pesticides) are a well-known group of legacy contaminants, which have been monitored and regulated in most parts of the world for the last four decades, being also referred as “regulated contaminants” (Jones and de Voogt, 1999; Lohmann et al., 2007). On the other hand, emerging contaminants (ECs) are chemical compounds that are not necessarily new, but are not or are only partly regulated and are not included in routine monitoring programs (Pintado-Herrera et al., 2016a).

Despite the availability of an important amount of data sets and long time-series for legacy contaminants, most of the data available refers to restricted areas and a shortage of off-shore datasets has been detected (Crise et al., 2015). Regarding emerging contaminants, although they have been increasingly studied in water, including drinking water, rivers, groundwater, wastewaters and effluents from wastewater treatment plants (WWTPs) since the 1990’s (Tijani et al., 2015 and references therein), studies focusing on the fate of emerging contaminants in the marine environment are rather scarce and the knowledge on their occurrence, fate and effects is still limited (Beretta et al., 2014).

As POPs and some groups of ECs sorb preferentially to suspended particulate matter, sequestration by sinking particles and burial in deep ocean sediment may represent a major sink for lipophilic contaminants (Dachs et al., 2002; Desforges et al., 2014; Sobek and Gustafsson, 2014). Concerning the Adriatic Sea, previous studies have suggested that the ultimate repository for contaminants are deep-sea areas located in the southern Adriatic where the cascading of the North Adriatic Dense Water (NAdDW) is able to quickly transfer suspended particles and, therefore, particle-binding contaminants, coming from the north Adriatic (Turchetto et al., 2007; Tesi et al., 2008; Combi et al., 2016; Langone et al., 2016).

Thus, the aim of this work was to investigate and compare levels and spatial patterns of selected groups of regulated and emerging contaminants in sediments from coastal and deep-sea areas in the Adriatic Sea in order to fully characterize the transfer and burdens of contaminants from coastal waters to the open sea along the Adriatic margin. We also aim to contribute with unprecedent data on the presence of emerging contaminants in the Adriatic Sea, filling the gap of information on the occurrence and off-shore levels of these substances. .

## Material and methods

### *Study area*

The Adriatic Sea (Figure 1) is a shallow semi-enclosed basin in Southern Europe. The Adriatic Sea is commonly divided into three sub-basins: the northern Adriatic, at the north of Ancona and with depths up to 100 m; the middle Adriatic, between Ancona and the Gargano Promontory, reaching depths of 270 m; and the southern Adriatic, from the Pelagosa Sill to the Otranto Strait, which includes the deepest area of the Adriatic Sea (the South Adriatic Pit, up to 1200m).

Freshwater input comes mainly from the Po River (northern Adriatic), which is responsible for the transport of approximately one-fourth of the sediment that enters the Adriatic Sea (Frignani et al., 2005). The remaining material is supplied by northern rivers draining the eastern and short, steep rivers draining the Apennine Mountains (Frignani et al., 2005). As a result of thermohaline factors and water dynamics, the material is exported southwards and the suspended material accumulates in a continuous belt along the coast, forming the late-Holocene mud wedge (Correggiari et al., 2001; Cattaneo et al., 2003).

During cold and dry winters, the northern Adriatic is subject to intense cooling associated with local wind forcing (Bora wind), resulting in the formation of the NAdDW, the densest water of the whole Mediterranean (Vilibić and Supić, 2005; Tesi et al., 2008). After its formation, the NAdDW spreads southwards, sinking along the bathymetric gradient and reaching deep regions from the southern Adriatic basin by a process of dense water cascading (Tesi et al., 2008; Chiggiato et al., 2016; Langone et al., 2016). The cascading of the NAdDW is responsible for the higher particle delivery in the southern Adriatic, playing a first order control on the particulate fluxes through the south-western Adriatic margin (Turchetto et al., 2007; Langone et al., 2016).

### *Sampling and sediment characteristics*

The sediment sampling was performed in October 2014 on board the O/V OGS Explora in transects perpendicular to the coast from Northern to Southern Adriatic (Figure 1). Surface sediment samples were collected along the Adriatic mud wedge, the Bari Canyon and the South Adriatic Pit by mini box corer or oceanic box corer. The top 0.5 cm of undisturbed sediment was sampled. Sediments were placed into pre-cleaned glass jars and stored at -20 °C.

Porosity ($\phi$) was calculated from the loss of water between wet and dry sediment according to equations suggested by Berner (1971), assuming a sediment density of 2.65 g $cm^{-3}$ and a water density of 1.027 g $cm^{-3}$. Grain size was determined after a pre-treatment with $H_2O_2$ and wet sieving at 63 μm to separate sands from fine fractions. Total nitrogen (TN) content were determined by elemental analysis (EA) of combusted aliquots with a Fison NA2000 EA, and organic carbon (OC) was measured on decarbonated samples (1 M HCl).

### *Analytical method and instrumental analyses*

The legacy and emerging compounds analyzed in the sediment samples, their respective log $K_{ow}$, main applications and sources are presented in Table 1. Sediments were extracted using an accelerated solvent extraction ASE 200 system (Dionex, USA) according to the extraction and in-cell clean-up method optimized by Pintado-Herrera et al. (2016a). Briefly, the extraction cells (11 mL) were prepared with 1 g of activated alumina (150°C for 16 hours; USEPA method 3610b) and 0.5 g of activated copper powder. Approximately 4 g of air-dried and milled sediment were homogenized with 1g of alumina and placed into the extraction cells. The extraction procedure consisted of three static extraction cycles using dichloromethane, where the samples were pre-heated for 5 minutes and extracted for 5 minutes in each cycle at a temperature of 100°C and a pressure of 1500 psi. The eluates were evaporated to dryness and re-dissolved in 0.5 mL of ethyl acetate. The final extracts were centrifuged (10000 rpm for 10 minutes) and filtered (0.22 μm) to remove possible interferences. The efficiency of the extraction method was evaluated by using standard reference material (marine sediment 1941b, National Institute of standards and Technology: NIST) for POPs and by spiking samples at three different concentrations (20, 100 and 200 ng $g^{-1}$) for ECs. Recovery percentages were between 70 and 100%. More specific details on this can be found at Pintado-Herrera et al. (2016a).

Separation, identification and quantification of target compounds were performed using gas chromatography (SCION 456-GC, Bruker) coupled to a triple quadrupole mass spectrometer equipped with a BR-5ms column (length: 30 m, ID: 0.25 mm, film thickness: 0.25 μm). The oven temperature was programmed to 70 ºC for 3.5 min, increasing at 25 ºC $min^{-1}$ to 180 ºC, increasing at 10 ºC $min^{-1}$ to 300 ºC, holding this temperature for 4 min. A derivatizing agent (*N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamid - MTBSTFA) was added to the samples to improve signal intensity and peak shape of some target compounds (e.g., BP3). Internal standards (mixture of deuterated compounds) were also included to account for the matrix suppression. Calibration curves were prepared for each target compound at different concentrations (from 5 to 500 ng $g^{-1}$). Target compounds were identified and quantified by comparison of retention times and two transitions of each analyte (one for quantification and one for confirmation) of the samples with external standard solutions. Procedural blanks were performed for each extraction series of 10 samples using alumina and analyzed in the same way as samples. Method detection limits (MDL) were determined for each analyte as 3 times the signal to noise ratio in spiked sediment samples and were between 0.003 and 0.54 ng $g^{-1}$ depending on the target compound.

*Inventories, total burdens, contaminant accumulation and risk assessment*

Inventories were calculated for surface sediment using the following equation:

$$Inventory = \sum C_i d_i \rho_i$$

where $C_i$ is the concentration of each contaminant in sediment sample $i$ (ng g$^{-1}$ dry weight), $d$ is the thickness of the sediment sampled (0.5 cm) and $\rho_i$ is the dry mass bulk density (g cm$^{-3}$). In order to calculate the total burdens (mass of contaminants), the Adriatic Sea has been divided in several boxes defined by different orientation of the coastline which, along with the general water circulation, controls the variability of sediment accumulation along the modern Adriatic mud wedge, as suggested by Frignani et al., 2005 (Figure S1 from Supplementary Material). The total burdens were calculated by multiplying the mean calculated inventories in surface sediments by the area of the boxes (Yang et al., 2012). According to the annual sediment accumulation rate (Tg y$^{-1}$) estimated by Frignani et al (2005), the annual contaminant accumulation (kg y$^{-1}$) for each box was also estimated.

For the preliminary risk assessment, the hazard quotients (HQs) for legacy and emerging contaminants were calculated using the measured environmental concentration (MEC) and the predicted non-effect concentration (PNEC), as follows:

$$HQ = MEC / PNEC$$

The PNEC values were either obtained from available literature or calculated using no observed effect concentrations (NOEC) from chronic toxicity bioassays or acute toxic endpoints (half maximal effective concentration, or EC50) and dividing toxicity data by a factor of 100 or 1000, respectively. Both, PNEC and calculated PNEC values, are presented in Pintado-Herrera et al. (2016b). Concentrations of target compounds in surface sediments presented in this work were used as MEC. For interpretation, $HQ < 0.1$ indicates no hazard, $0.1 < HQ < 1$ a low hazard, $1 < HQ > 10$ a moderate hazard, and $HQ > 10$ a high hazard ( Lemly, 1996; Chen et al., 2010).

### *Statistical analyses*

To explore the relationship between the variables, Pearson's correlation coefficient at 0.05 significance level was applied. Linear discriminant analysis was performed using the statistical package "MASS" (Venables and Ripley, 2002). Discriminant analysis is a statistical procedure for identifying boundaries between groups of samples based on quantitative predictor variables (Mourier et al., 2014). In our case, the variables used were the contaminant concentrations, and the percentage of OC and fine sediments (mud, as sum of the silt and clay fractions), while the groups were the northern, central, and southern Adriatic Sea sectors. Data were z-scoring standardized in order to eliminate the influence of different units and make each determined variable have equal weighting. Statistical data analyses were performed with R software (R Core Team, 2013).

## Results

### *Sediment characteristics*

Fine fractions (silt and clay) were predominant in sampled sediments accounting for ~50 to ~99% (Table 2 and Tables S1 to S3 from Supplementary Material). OC was relatively low and limited in variability within the Adriatic mud-wedge sediments, varying between 0.6 and 1.6%. These levels are consistent with previous data on OC content found in the region (Tesi et al., 2007, 2013; Turchetto et al., 2007). In general, OC and C/N ratio were higher in the northern section (1.0 ± 0.2% and 9.6 ± 0.8, respectively), especially in the samples closer to the Po River prodelta. The lowest OC and C/N values were detected in sediments off coast from central (0.5 to 0.9% and 7.6 to 9.5, respectively) and southern (0.5 to 0.8% and 7.7 to 9.4, respectively) areas.

### *Concentrations of contaminants in sediments*

Among all target contaminants considered in this study, PAHs were by far the most prevalent compounds in surface sediments from the Adriatic Sea, with $\sum_{16}$ PAHs ranging from 38.8 to 572 ng $g^{-1}$ (Table 2 and Tables S1 to S3 from Supplementary Material). The highest  concentrations (presented as the mean concentration ± standard deviation - SD) were detected in the northern section (300 ±101 ng $g^{-1}$), followed by the central  (115.3±27.4 ng $g^{-1}$) and southern sections (107.4 ±64.2 ng $g^{-1}$). High molecular PAHs (HMW; 4–6 rings) accounted for 65 to 95% of total PAHs.  The ratio between low- and high-molecular weight PAHs (LMW and HMW, respectively) ranged from 0.1 to 0.5, while the ratios between indeno[1,2,3-cd]pyrene and benzo[g,h.i]perylene (Ip/Ip+Bper), fluoranthene and pyrene (Flt/Pyr and Flt/Flt+Pyr), and benz[a]anthracene and chrysene (Ba/Ba+Chr) ranged from 0.2 to 0.6, from 0.9 to 1.5 and from 0.3 to 0.5, respectively.

UV filters and nonylphenol (NP) were next in terms of concentration after PAHs. They ranged from <LOD (below limit of detection) to 40.7 ng $g^{-1}$. Octocrylene was the most abundant UV filter (16.3±9.6 ng $g^{-1}$, 7.6±6 ng $g^{-1}$ and 6.8±4 ng $g^{-1}$ in the northern, central and southern sectors, respectively), followed by EHMC (4.5±2.2 ng $g^{-1}$, 2.4±1 ng $g^{-1}$ and 3.2±1.4 ng $g^{-1}$ in the northern, central and southern sectors, respectively). Both compounds were detected in all the sediment samples. Conversely, BP3 was detected at very low concentrations (0.05±0.05 ng $g^{-1}$, 0.02±0.02 ng $g^{-1}$ and 0.06±0.06 ng $g^{-1}$ in the northern, central and southern sectors, respectively) and only in ~50% of the sediment samples. Regarding NP isomers, their higher concentrations were detected in the northern sector (17±8.4 ng $g^{-1}$), while the concentrations in the central and southern sectors were very similar, with mean values of 6.3±4.5 ng $g^{-1}$ and 6.7±4.5 ng $g^{-1}$, respectively.

Concentrations of fragrances ranged from <LOD to 24.3 ng $g^{-1}$ (Table 2 and Tables S1 to S3 from Supplementary Material). In general, tonalide was present in higher concentrations (6.2±4.6 ng $g^{-1}$, 2.9±2.2 ng $g^{-1}$ and 6.0±2.7 ng $g^{-1}$ in the northern, central and southern sectors of the Adriatic Sea, respectively) in the sediment samples in comparison to galaxolide (4.3±2.8 ng $g^{-1}$, 1.9±1.5 ng $g^{-1}$ and 4.0±2.7 ng $g^{-1}$ in the northern, central and southern sectors, respectively; Table 2). Galaxolide to tonalide ratios ranged from 0 to 5.4 (1±0.9).

Lastly, the organochlorine compounds (PCBs and DDTs) were detected at the lowest concentrations and presented a similar range of concentrations. Total PCBs ($\sum_5$PCBs) and total DDTs (*p,p'*DDD, *p,p'*DDE and *p,p'*DDT) in surface sediments varied between 0.05 and 4.2 ng $g^{-1}$ and between 0.05 and 4.3 ng $g^{-1}$ respectively (Table 2 and Tables S1 to S3 from Supplementary Material). Similarly to the rest of target compounds, they were also detected in higher concentrations in the northern box (2.0±0.9 ng $g^{-1}$) followed by the middle (0.7±0.4 ng $g^{-1}$) and southern (0.4±0.3 ng $g^{-1}$) boxes. Although total DDTs were also higher in the northern sector (1.6±1.0 ng $g^{-1}$), they were very similar between the central and southern boxes (0.6±0.2 and 0.7±0.3 ng $g^{-1}$, respectively). While DDE and DDD were ubiquitous in sediments from the Adriatic Sea, DDT was detected only in 20% of the samples.

*Inventories, total burdens and contaminant accumulation*

The estimated inventories, burdens and contaminant accumulation in the Adriatic Sea are presented in Table 2. As expected from concentration data, PAHs ($\sum_{16}$PAHs) presented the highest inventories (mean value and SD of 810±380 ng $cm^{-2}$ among the three sectors), followed by octocrylene and NP (47±19 ng $cm^{-2}$ and 46±20 ng $cm^{-2}$, respectively). The total inventories of the organochlorine compounds were very similar, with 4.8±3 ng $cm^{-2}$ and 4.5±2 ng $cm^{-2}$ for PCBs ($\sum_5$PCBs) and DDTs (∑*p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE), respectively. The mean inventory of the fragrances was approximately 15±4 ng $cm^{-2}$ for galaxolide and 22.5±5.5 ng $cm^{-2}$ for tonalide. Regarding the other UV filters, EHMC presented a mean inventory of 16±4.5 ng $cm^{-2}$ and BP3 of 0.2±0.1 ng $cm^{-2}$. Estimated burdens in the whole Adriatic basin were nearly 15,000 kg for PAHs, 900 kg for octocrylene, 765 kg for NP, 424 kg for tonalide, 330 kg for EHMC, 275 kg for galaxolide, 80 kg for PCB and DDT, and 4 kg for BP3. Total annual contaminant accumulation in the Adriatic Sea ranged from 0.2 for BP3 kg $y^{-1}$ to ~7800 for PAHs kg $y^{-1}$. The total annual accumulations were similar for NP and octocrylene (~450 kg $y^{-1}$) and the organochlorine compounds (~45 kg $y^{-1}$). EHMC, galaxolide and tonalide presented similar total annual accumulation as well (~140 to 210 kg $y^{-1}$).

## Discussion

*Comparison of the occurrence, sources and distribuion of legacy and emerging contaminants in sediments*

Figure 2 illustrates the occurrence of emerging contaminants in sediments from transition and coastal areas around the world, including our sampling area (Adriatic Sea). So far, only a few studies have reported the levels of emerging contaminants in sediments, especially in marine and deep-sea ecosystems. In comparison to the Po River, the fragrances tonalide and galaxolide and the endocrine disruptor NP presented far lower mean concentrations in our study (Viganò et al., 2015). Overall, NP concentrations were far lower in comparison to other areas, except for coastal areas in southern France (Hong et al., 2009). Tonalide and galaxolide levels were also lower when compared to semi-enclosed coastal areas such as Cádiz Bay (Pintado-Herrera et al., 2016a) and  Hempstead Bay (Fisher et al., 2016), but comparable to the levels reported in urbanized coastal areas from China (Pintado-Herrera et al., 2016b) and Korea (Lee et al., 2014). The concentrations of the UV filters EHMC and octocrylene in our study were far lower than those reported in the Eastern Mediterranean (Amine et al., 2012), while EHMC presented similar concentrations to those detected in touristic areas, as southern France (northwestern Mediterranean coast; Amine et al., 2012) and urbanized areas, as the Pearl River Estuary, China (Pintado-Herrera et al., 2016b).

More detailed information on the concentrations and spatial trends of target contaminants in the Adriatic Sea is presented in Figures S2 to S6 from Supplementary Material and revealed a similar pattern, with decreasing concentrations from the Po River prodelta southward to the Otranto channel and in deep areas from the South-Western Adriatic Margin (SWAM). The Po River is the largest and most important Italian river, draining large agricultural and highly industrialized areas, inhabited by about 15 million of people, and being responsible for the transport of approximately one-fourth of the sediment that enters the Adriatic Sea (Frignani et al., 2005; Romano et al., 2013; Tesi et al., 2007). Thus, the Po River appears to be the major contributor for the inputs of legacy and emerging contaminants to sediments in the Adriatic Sea.

Although contaminant concentrations are generally lower in the central and southern sectors, some increased concentrations can be noticed especially around Ancona and Bari, which are areas with intense human activities, sheltering two of the most important commercial and passenger harbors of the Adriatic Sea (Mali et al., 2015), that are local sources of contaminants. PAHs and PCBs have been previously detected at higher concentrations in these areas, especially around the Bari port (Guzzella and Paolis, 1994; Mali et al., 2015; Combi et al., 2016). As to the fragrances, their application in a broad range of personal care products, including soaps and detergents (OSPAR Commission, 2004), may help explaining their presence in these areas. Fragrances and UV filters also presented somewhat higher levels in touristic coastal areas in the central and southern Adriatic, which may be related to the direct input from recreational activities (bathing, swimming) (Pintado-herrera et al., 2016b). Additionally, the proximity to major cities (e.g. Ancona and Bari) and tourist facilities results in an increased load of ECs from WWTPs effluents, which, in turn, represent one of their major sources to the marine environment (Chase et al., 2012; Villa et al., 2012). Previous studies also related the presence of fragrances and UV filters to both the proximity to tourist areas and WWTPs discharges (Downs et al., 2015; Villa et al., 2012).

Both, legacy and emerging contaminants were also detected in deep sediments within the SWAM. Although the contaminant contents are not at hazardous levels, the detection of highly chlorinated PCBs (Combi et al., 2016) and other highly hydrophobic compounds (e.g. octocrylene and benzo[g,h,i]perylene) reinforces the hypothesis that the cascading of the NAdDW would be able to transfer particle-binding contaminants coming from the north Adriatic and testifies that the impact of anthropic contamination by inland inputs may not be confined to the proximity of the river mouths but can be exported at long distance (600 km in the Adriatic) and toward the deep ocean (down to 1200 m).

Statistical analysis of the data reveals that concentrations of both legacy and emerging contaminants (PAHs, PCBs, DDTs and NP) were positively correlated to OC ($r \geq 0.5$; $p$ value $\leq 0.01$), suggesting that their spatial distribution is dependent on the OC content of sediments. NP was strongly correlated to legacy contaminants ($r \geq 0.6$; $p$ value $< 0.001$) and the UV filters (EHMC and octocrylene) were also correlated ($r = 0.5$; $p$ value $< 0.001$), confirming these compounds present similar spatial distribution and may derive from similar input sources. The discriminant analysis explained the data variance (83.3% and 16.7% for LD1 and LD2). The scatterplot of the two discriminant functions (LD1 and LD2) shows that the north sector is better separated than the center and south (Figure 3) and PCBs, PAHs, EHMC and OC were the variables that most contributed to the group differentiation. According to the confusion matrix, which evaluates the consistency of classification of samples into groups (Mourier et al., 2014), the accuracy of the classification appears to be relatively high, since 70%, 80% and 90% of the samples were well reclassified within the predefined groups (central, southern and northern areas, respectively). Although PCBs, PAHs, and EHMC were the compounds of highest importance for separating the areas, the stronger discrimination of the northern sector can be also related to the higher concentrations detected for most contaminants in this area, especially close to the Po River prodelta. On the other hand, the spatial distribution of ECs was generally not as clear as the distribution detected for legacy contaminants, especially in the central and southern Adriatic, which may explain the weak differentiation among these groups.

A more detailed analysis of each class of contaminants shows different compositional patterns. Regarding legacy contaminants, the Adriatic Sea sediments were depleted in LMW (2–3 rings) and enriched in HMW (4–6 rings) PAHs (Tables S1 to S3 from Supplementary Material), and Ip/Ip+Bper, Flt/Pyr, Flt/Flt+Pyr and Ba/Ba+Chr ratios indicate PAHs sources from biomass and petroleum combustion (Figure S7 from Supplementary Material). These ratios corroborated the pyrolytic origin of PAHs in the sediment samples from the Adriatic Sea, which is in agreement with previous research accomplished in the Adriatic Sea (Magi et al., 2002). Considering the organochlorine compounds, the most abundant PCB congeners were PCB 138 followed by PCB 180, while among compounds of DDT family, DDE was the prevalent isomer. Although PCBs and DDTs have been banned in Italy since the late 1970's (Tolosa et al., 1997; Binelli and Provini, 2003), these contaminants are still present in recent sediments from the Adriatic Sea. Indeed, previously contaminated soils around the drainage basin of the Po River can be slowly released over time  and seem to be continuously contaminating waterbodies in the north of Italy, ultimately accumulating in the Adriatic Sea sediments (Frignani et al., 2004; Combi et al., 2016).

Different ratios could be also established for emerging contaminants such as fragrances. Galaxolide is commercially the most used polycyclic musk fragrance, followed by tonalide (Villa et al., 2012). In 2000, the production of galaxolide and tonalide in Europe was estimated on 1427 tonnes and 358 tonnes, respectively (OSPAR Commission, 2004). For this reason, galaxolide is usually detected in higher concentrations in continental, marine and transitional ecosystems, as well as in wastewaters (Chase et al., 2012; Pintado-Herrera et al., 2016a; Sumner et al., 2010). However, tonalide was found in relatively higher levels than galaxolide in Adriatic Sea, presenting galaxolide to tonalide ratios in general lower than the commercial ratio of about 4:1 (OSPAR Commission, 2004). Although both compounds present similar physico-chemical properties (e.g., log $K_{ow}$ 5.7-5.9 and vapor pressure 0.068 – 0.073; Chase et al., 2012), previous studies suggested that galaxolide is degraded more easily than tonalide  (Lee et al., 2014), and that tonalide preferentially adsorbs to particulate matter (Dsikowitzky et al., 2002), which are the most likely reasons why tonalide is ubiquitous in the Adriatic Sea sediments. Tonalide has also been detected in higher concentrations in some of the sediment samples from the Po River (Viganò et al., 2015) and Sacca di Goro Lagoon (Casatta et al., 2015).

Octocrylene was the predominant UV filter, followed by EHMC and BP3. Octocrylene is one of the most used UV filters in Europe, being present in over 80% of sunscreen products, while EHMC and BP3 can be found, respectively, in ~50% and ~20% of the products (De Groot and Roberts, 2014; Rastogi, 2002). The octanol-water partition coefficient is an indicator of the environmental fate of the UV-filters, translating how they are distributed between sediments/lipids and the aqueous phase (Ramos et al., 2015). Octocrylene is nowadays of great concern since it is a highly lipophilic compound, stable, and resistant to sunlight degradation (Gago-Ferrero et al., 2013). EHMC is also a very hydrophobic compound while BP3 is slightly soluble in water (Table 1), making it less likely to be encountered in marine sediments.

NP isomers presented the highest concentrations among the emerging contaminants analyzed in our work. NP is an endocrine disrupting compound frequently detected in high concentrations in continental, marine and transitional waters (Pojana et al., 2007; Lara-Martín et al., 2014; Meffe and de Bustamante, 2014). Surfactants are among the most produced and consumed substances in the world and, among their degradation products, nonylphenol presents hydrophobic properties causing a preferential accumulation in sediments (Pintado-Herrera et al., 2016a; Pojana et al., 2007). High concentrations of NP in comparison to other classes of contaminants in sediments from Venice lagoon (47 – 192 ng $g^{-1}$) have been attributed to the proximity to municipal and industrial wastewaters treatment plants (Pojana et al., 2007).

Fragrances, UV filters and NP can be found in relevant concentrations in both, influent and effluent wastewaters, as most WWTPs are not designed to treat these types of substances (Chase et al., 2012; Langford et al., 2015). Because of their hydrophobic properties, the removal of emerging compounds during wastewater treatment is mainly related to their sorption on sludge solids (Carballa et al., 2004; Langford et al., 2015). For instance, the removal efficiency of NP after wastewater treatments is around 50 – 80% (Melo-Guimarães et al., 2013; Stasinakis et al., 2013), while the removal efficiency of tonalide and galaxolide can be around 85% (Carballa et al., 2004). Consequently, a significant fraction of emerging compounds is constantly discharged through WWTPs and untreated wastewater into the aquatic environment, leading to a widespread contamination of continental, transitional and marine waters (Chase et al., 2012; Sumner et al., 2010; Villa et al., 2012). Because of their hydrophobic properties, most of these compounds are sorbed to some extent on suspended solids during wastewater treatment and as a result they can also be found in sludge.

*Burden estimation, contaminant accumulation, and preliminary risk assessment*

Inventories and burden estimations represent the integrated mass of the compounds of interest and can be used as a tool to understand a suitable insight for further behavior of the compounds per unit area (Kim et al., 2008; Song et al., 2004). Inventories and total burdens (total mass of contaminants) were calculated with reference to the top 0.5-cm of sediment, which means that the actual inventories and total burdens would be much larger than estimated for the Adriatic Sea. Legacy contaminants presented the highest total burdens in the northern sector (40-45%) of the Adriatic Sea, while the total burdens of BP3 and the fragrances were higher in the southern sector (45-50%). Estimated burdens in the southern Adriatic are especially influenced by the larger total area in the deep-sea in comparison to the coastal areas (Figure S1 from Supplementary Material). Total burdens in the central Adriatic ranged from 20 to 40%, with the highest values corresponding to NP and octocrylene. The similar burdens between the central and southern sectors reinforces the weak separation detected by the discriminant analysis and the presence of local sources in these areas.

Estimated annual contaminant accumulation highlights that legacy and emerging contaminants accumulate preferentially in the northern Adriatic (40 to 60% of the total annual contaminant accumulation), followed by the central (25 to 38%) and southern Adriatic (8 to 30%). Altogether ~ 12% of the legacy and emerging contaminants annually entering the Adriatic Sea accumulate in the deep Adriatic basin, which has been previously suggested to be an additional repository for sediments (Frignani et al., 2005; Turchetto et al., 2007; Langone et al., 2016). The annual contaminant accumulation and burden estimation are in agreement with the spatial distribution trends of legacy and emerging contaminants along the Adriatic Sea, corroborating the hypothesis that the Po River represents the major input sources of most contaminants to the Adriatic Sea.

In order to estimate and evaluate potential ecotoxicological risks of these chemicals in sediments from the Adriatic Sea, we calculated the hazard quotients (HQs) for individual legacy and emerging contaminants (Table S4). Emerging contaminants present no significant ecological risk in sediments of the Adriatic Sea except for the UV filter EHMC, which poses moderate risk for sediment-associated biota. The HQs suggested a high risk of adverse effects to biota related to total PAHs, *p,p'*-DDE and PCBs in the northern sector and related to dibenzo[a,h]anthracene and *p,p'*-DDE in the central and southern sectors. In any case, it is necessary to consider that environmental matrices contaminated with diverse groups of pollutants are complex in terms of understanding the interaction mechanisms among different compounds; previous studies have demonstrated that the presence of many chemicals may have addictive toxicological effect (Cristale et al., 2013).

Individual HQs were combined and divided by the number of HQs, similarly to the approach proposed by Long et al. (2006) for the assessment of mean Sediment Quality Guidelines (SQGs), in order to investigate the overall risk of contaminants in sediments from the Adriatic Sea. The combined HQs (∼3 and ∼4, respectively) for central and southern Adriatic Sea suggest a moderate hazard for sediment-associated biota, while in the northern Adriatic section combined HQ suggests high ecotoxicological hazard (HQ = ∼10). Along with the fact that individual HQs suggested high ecotoxicological risk for organisms for several legacy compounds, we can infer that legacy, and to a lesser extent emerging contaminants present in sediments from the northern Adriatic Sea are likely to pose an immediate or long-term hazard to resident biota. In any case, more specific data on the toxicity of emerging contaminants over marine species is needed to refine further environmental risk assessments on UV filters, fragrances and many other new chemicals.

## Conclusions

Emerging and legacy contaminants were investigated in surface sediments along the modern Adriatic mud wedge and in selected deep-sea areas from the South-Western Adriatic Margin (SWAM). To the best of our knowledge, this is the first study on ECs occurrence, levels and distribution at an oceanic basin scale. Spatial trends of legacy and emerging contaminants revealed a similar pattern, with decreasing concentrations from the Po River prodelta southward, suggesting the Po River as the major contributor of contaminants to sediments in the Adriatic Sea. This inference is further corroborated by the distribution patterns for OC and annual contaminant accumulation along the Adriatic Sea, with higher values consistently detected in the northern section. A significant presence of emerging compounds has been detected in the southern Adriatic, especially fragrances and UV filters, most likely related to diffuse sources (e.g. tourist activities and WWTPs discharges).

The hypothesis that the deep-sea areas in the southern Adriatic may represent the final repository for contaminants entering this system has been reinforced by the annual contaminant accumulation estimated for this basin. The transfer of contaminants from coastal waters to the open sea has been related to the cascading of the North Adriatic Dense Water (NAdDW) in deep-sea areas in the southern Adriatic, which would be able to quickly transport suspended sediments (and, therefore, particle-binding contaminants) during these episodic events. Further studies on the occurrence, distribution and fate of ECs in off-shore aquatic settings and at different latitudes are encouraged to achieve a better understanding on their environmental behavior on a global scale.

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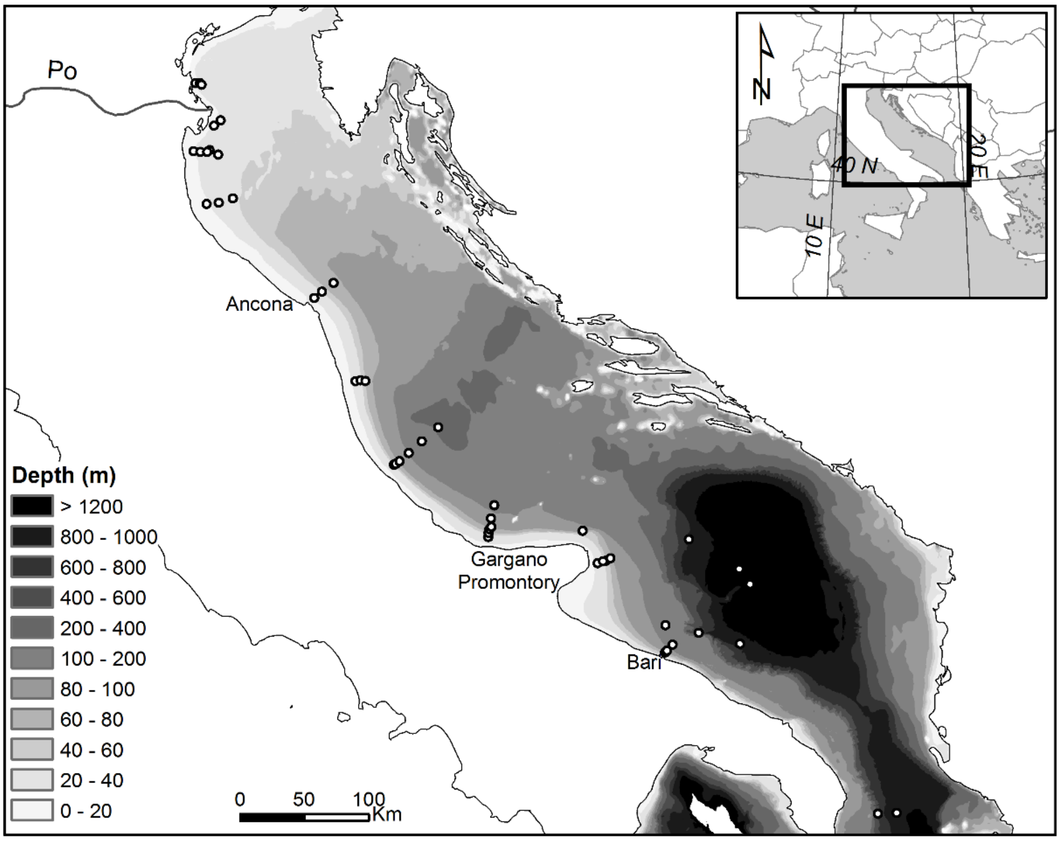

**Figure 1.** Map of the study area showing the sampling stations and the bathymetry of the Adriatic Sea.

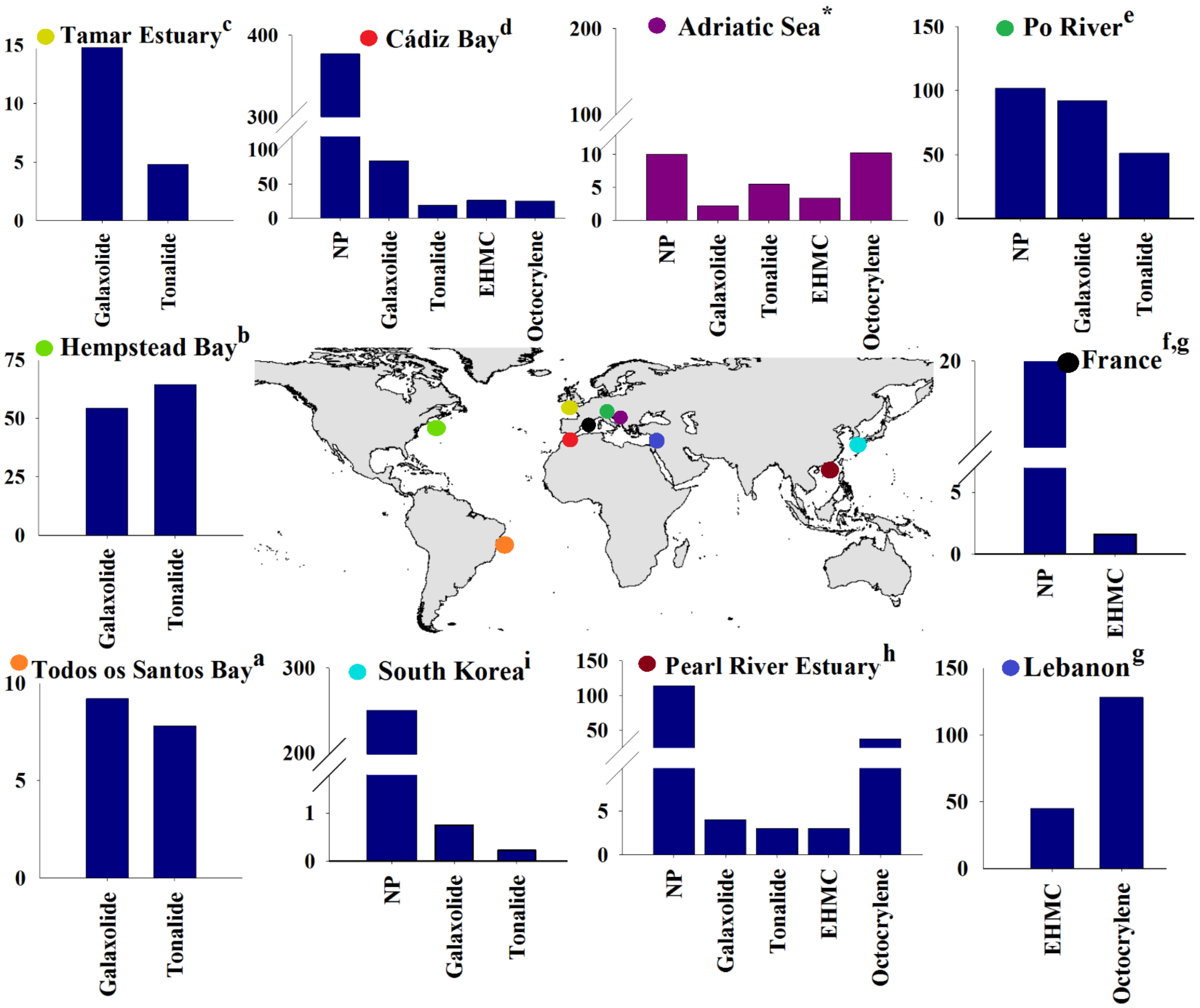

**Figure 2.** Comparison of emerging contaminants concentrations (mean value, ng $g^{-1}$) in sediments from transition and coastal areas around the world. *: Present study; [a]Beretta et al. (2014); [b]Fisher et al. (2016); [c]Sumner et al. (2010); [d]Pintado-Herrera et al. (2016a); [e]Viganó et al. (2015); [f]Hong et al. (2009); [g]Amine et al. (2012); [h]Pintado-Herrera et al. (2016b); [i]Lee et al. (2014).

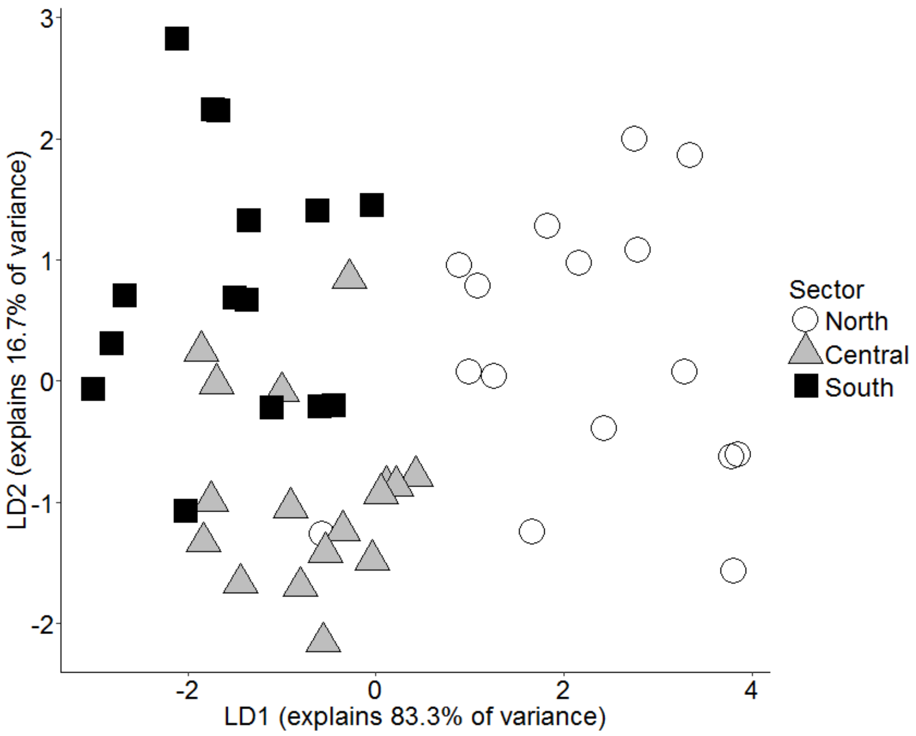

**Figure 3.** Discriminant analysis scatterplot on legacy and emerging compounds in the northern, central and southern sections of the Adriatic Sea.

**Table 1.** Legacy and emerging contaminants analyzed with their respective log $K_{ow}$, main applications and sources.

| Group | Analyte | Log$K_{ow}$ | Application | Sources |
|---|---|---|---|---|
| PAHs | Naphthalene | 3.98 | - | Product of the incomplete combustion of fossil fuels and organic material, natural and anthropogenic petroleum spillages |
| | Acenaphthylene | 3.37 | | |
| | Acenaphthene | 4.07 | | |
| | Fluorene | 4.27 | | |
| | Anthracene | 4.50 | | |
| | Phenanthrene | 4.46 | | |
| | Pyrene | 4.88 | | |
| | Fluoranthene | 4.90 | | |
| | Benzo[a] anthracene | 5.63 | | |
| | Chrysene | 5.63 | | |
| | Benzo[b] fluoranthene | 6.04 | | |
| | Benzo[k] fluoranthene | 6.21 | | |
| | Benzo[a]pyrene | 6.06 | | |
| | Dibenzo[a,h] anthracene | 6.86 | | |
| | Indeno[1,2,3-cd]pyrene | 6.58 | | |
| | Benzo[g,h,i] perylene | 6.78 | | |
| PCBs | PCB52 | 5.9 | Dielectric fluids in transformers and capacitors, heat-exchange liquids, hydraulic fluids, flame retardants, lubricants, waxes | Current sources include leaching from contaminated soils, urban runoff, industrial and domestic wastewaters and volatilization |
| | PCB138 | 6.6 | | |
| | PCB153 | 6.7 | | |
| | PCB180 | 6.9 | | |
| | PCB101 | 6.1 | | |
| DDTs | *p,p'*-DDT | 6.9 | Pesticides and insecticide formulations | Leaching of cultivated land and contaminated soils and volatilization |
| | *p,p'*-DDD | 6.0 | | |
| | *p,p'*-DDE | 6.5 | | |
| Fragrances | Galaxolide | 5.9 | Cosmetics and personal care products, such as perfumes, soaps, detergents, shampoos, etc. | Wastewater treatment plants, untreated wastewater, direct input from recreational activities (bathing, swimming). |
| | Tonalide | 5.7 | | |
| UV-filters | Octocrylene | 6.88 | Cosmetics and personal care products such as sunscreen lotions, hair sprays, lip balms, conditioners, etc. | |
| | EHMC | 5.8 | | |
| | BP3 | 3.8 | | |
| Endocrine disruptors | NP isomers | 5.7 | Degradation product from nonylphenol ethoxylates | Municipal and industrial wastewaters |

**Table 2.** Sediment chemical data summaries for the Adriatic Sea. Data show the mean, standard deviation (SD), minimum and maximum concentrations (ng $g^{-1}$), the estimated burdens of contaminants (kg), the annual contaminant accumulation (kg $y^{-1}$) and the inventories (ng $cm^{-2}$) for each area (northern, central and southern Adriatic). Fine sediments (silt and clay) and OC are presented as %.

| | | Min | Max | Mean | SD | Burdens | Accumulation | Inventories |
|---|---|---|---|---|---|---|---|---|
| Northern Adriatic | Silt + clay | 94.0 | 99.5 | 98.0 | 1.0 | - | - | - |
| | OC | 0.6 | 1.6 | 1.0 | 0.2 | - | - | - |
| | C/N | 8.0 | 12.5 | 9.6 | 0.8 | - | - | - |
| | PAHs | 103.6 | 572 | 300 | 101.0 | 5400 | 4330 | 1383 |
| | PCBs | 0.3 | 4.3 | 2.0 | 0.9 | 35 | 30 | 9.0 |
| | DDTs | 0.2 | 4.3 | 1.6 | 1.0 | 32 | 25 | 7.3 |
| | Tonalide | 1.3 | 24.3 | 6.2 | 4.6 | 85 | 85 | 38.7 |
| | Galaxolide | 0.05 | 11.9 | 4.3 | 2.8 | 50 | 58 | 11.8 |
| | Octocrylene | 4.0 | 40.7 | 16.3 | 9.6 | 260 | 230 | 75.8 |
| | BP3 | <LOD | 0.23 | 0.05 | 0.05 | 1.5 | 0.8 | 0.3 |
| | EHMC | 1.0 | 10.4 | 4.5 | 2.2 | 115 | 68 | 23.0 |
| | NP | 3.2 | 40.7 | 17.0 | 8.4 | 265 | 235 | 75.0 |
| Central Adriatic | Silt + clay | 89.0 | 99.6 | 98.3 | 1.5 | - | - | - |
| | OC | 0.5 | 0.9 | 0.7 | 0.1 | - | - | - |
| | C/N | 7.6 | 9.5 | 8.5 | 0.4 | - | - | - |
| | PAHs | 62.0 | 166.0 | 115.3 | 27.4 | 4800 | 2640 | 562.5 |
| | PCBs | 0.1 | 1.2 | 0.7 | 0.4 | 28 | 16 | 3.4 |
| | DDTs | 0.1 | 1.0 | 0.6 | 0.2 | 23 | 13 | 2.7 |
| | Tonalide | 0.9 | 13.6 | 3.0 | 2.2 | 128 | 70 | 13.0 |
| | Galaxolide | <LOD | 7.3 | 1.9 | 1.5 | 87 | 46 | 2.8 |
| | Octocrylene | 0.8 | 33.7 | 7.6 | 6.0 | 370 | 187 | 38.7 |
| | BP3 | <LOD | 0.1 | 0.02 | 0.02 | 1 | 1 | 0.1 |
| | EHMC | 0.9 | 6.9 | 2.4 | 1.0 | 104 | 56 | 11.6 |
| | NP | <LOD | 19.2 | 6.3 | 4.5 | 298 | 153 | 31.3 |
| Southern Adriatic | Silt + clay | 52 | 99.6 | 91.8 | 9.0 | - | - | - |
| | OC | 0.5 | 0.8 | 0.7 | 0.1 | - | - | - |
| | C/N | 7.7 | 9.4 | 8.4 | 0.5 | - | - | - |
| | PAHs | 38.8 | 368.5 | 107.4 | 64.2 | 3230 | 890 | 482.2 |
| | PCBs | <LOD | 0.8 | 0.4 | 0.3 | 14 | 4 | 1.8 |
| | DDTs | 0.3 | 1.5 | 0.7 | 0.3 | 24 | 7 | 3.0 |
| | Tonalide | 0.6 | 13.4 | 6.0 | 2.7 | 210 | 56 | 26.0 |
| | Galaxolide | 0.2 | 16.0 | 4.0 | 2.7 | 138 | 38 | 16.4 |
| | Octocrylene | 0.9 | 19.0 | 6.8 | 4.0 | 265 | 70 | 27.0 |
| | BP3 | <LOD | 0.18 | 0.06 | 0.06 | 2 | 1 | 0.2 |
| | EHMC | 1.3 | 10.0 | 3.2 | 1.4 | 108 | 30 | 14.0 |
| | NP | 0.5 | 31.8 | 6.7 | 4.5 | 200 | 55 | 30.6 |