



Phthalates, organotin compounds and *per*-polyfluoroalkyl substances in semiconfined areas of the Spanish coast: Occurrence, sources and risk assessment

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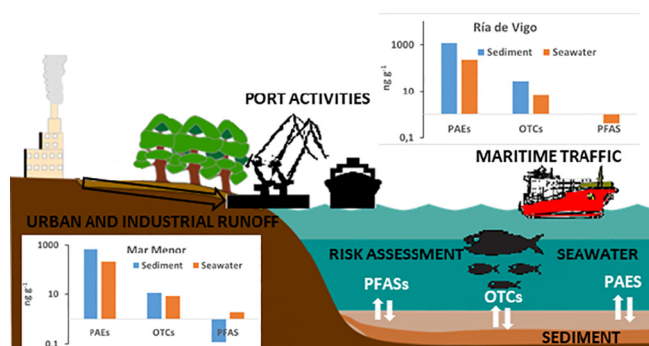
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HIGHLIGHTS

- The ubiquity of PFAS, OTCs and PAEs was confirmed in coastal areas.
- TBT concentrations in seawater were above MAC value of WFD.
- High ecological risk: TBT, BBP, DBP and DEP in sediments; TBT in seawater.
- No correlation between seawater-sediment distributions was found.
- Monitoring of PFAS, OTCs and PAEs is recommended in coastal areas.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work two sensitive areas of the Spanish coast located in the Atlantic (Ria de Vigo) and Mediterranean (Mar Menor lagoon) have been studied regarding their contamination by phthalates, organotin compounds and *per*-polyfluoroalkyl substances (seawater and sediments) in two different campaigns (spring and autumn in 2015). PFAS and OTCs were detected in seawater and sediments at low concentrations (few ng L⁻¹ or ng g⁻¹), whereas PAEs were detected at levels two orders of magnitude higher, particularly in Mar Menor lagoon due to its semi-confined characteristics. However, PAEs and OTCs concentration in sediments were higher in Ria de Vigo than in Mar Menor lagoon as a consequence of the influence of the important urban nuclei and port in that area.

The ecological risk assessment revealed that in both areas tributyltin, dibutyltin and diethylphthalate pose a significant risk in sediments, whereas in seawater tributyltin in both areas resulted in a high risk.

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) organotin compounds (OTCs) and phthalates (PAEs) are considered global environmental contaminants due to their wide usages, resistance to

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List of acronyms

AA-EQS	Annual Average-Environmental Quality Standard
BBP	butylbenzylphthalate
DBP	Dibutylphthalate
DBT	Dibutyltin
DEHP	Bis (2-ethylhexyl) phthalate
DEP	Diethylphthalate
DMP	Dimethylphthalate
DOP	Di-n-octylphthalate
DPhT	Diphenyltin
DPSE	Dispersive Solid-Phase Extraction
EPA	Environmental Protection Agency
HS-SPME	Headspace Solid-Phase Microextraction
MAC	Maximum admissible concentration
MBT	Monobutyltin
MEC	Measured Environmental Concentration
MPhT	Monophenyltin
MLs	Method Quantitation Limits
MSFD	Marine Strategy Framework Directive
MSPD	Matrix solid-phase dispersion
N-EtFOSA	N-ethylperfluorooctanesulfonamide
N-MeFOSA	N-methylperfluorooctanesulfonamide
OTCs	Organotin Compounds
PAEs	Phthalates
PFAS	Per- and polyfluoroalkyl substances
PFOA	Perfluoro-n-octanoic acid
PFOS	Perfluoro - 1 - octanesulfonate
PFOSA	Per-fluoro - 1 - octanesulfonamide
PNEC	Predicted no-effect concentration
POP	Persistent Organic Pollutant
RQ	Risk quotient
RQex	Risk quotient for the worst case scenario
TBT	Tributyltin
TeBT	Tetrabutyltin
TOC	Total Organic Carbon
TPhT	Triphenyltin
UAE	Ultrasonic Assisted Extraction
VALLME	Vortex Assisted Liquid-Liquid Microextraction
WFD	Water Framework Directive

degradation, bioaccumulation, toxicity, and persistence (Devos et al., 2012; Taniyasu et al., 2013).

Per- and polyfluoroalkyl substances (PFAS) are simultaneously hydrophobic and lipophobic anthropogenic chemicals, thermally and chemically stable. The food-packaging, textile, electroplating, firefighting, semiconductor industry, precious metals and coating industry emissions are some of their most important sources (Qi et al., 2016). OTCs, such as tributyltin (TBT), are persistent organic pollutants that result of different anthropogenic activities (antifouling agents in ship paints, biocides in polymers, textiles etc.) being the most heavily used organometallic compounds in the world; (Cole et al., 2015; WHO, 2006). The toxicity and endocrine disruption potential of these chemicals have been demonstrated even at very low levels ($<1 \text{ ng L}^{-1}$) (Devos et al., 2012; OSPAR-Commission, 2011). PAEs are esters of the phthalic acid, classified as endocrine disruptors (ECHA, 2019; European Commission, 2018), and used in the manufacture and processing of plastic products such as plasticizers in a very broad range of industrial applications. The phthalate most frequently used is bis (2-ethylhexyl) phthalate (DEHP) together with benzyl butyl phthalate (BBP), especially in PVC industry, but also in paint, cosmetic or pesticides industries (Liu et al., 2013). PAEs account for approximately 92% of produced plasticizers worldwide (Paluselli et al., 2018b). PAEs are not chemically bound to the plastics, and therefore they can be easily released to the environment.

The common source of PAEs OTCs and PFAS compounds is their use as plastic additives. Phthalates (PAEs) are one of the most relevant plastic additives, which are used as plasticizers to improve flexibility and durability, added at 10–80% w/w; organotin compounds (OTCs) are used as stabilizers (0.1–10%) or also as biocides, and per-polyfluorinated compounds used to produce fluoropolymers like polytetrafluoroethylene (PTFE) and perfluoroalkoxy polymer (PFA) (non-stick plastics). The occurrence of these compounds has been previously confirmed in the marine environment (Hermabessiere et al., 2017), mainly in seawater (Centineo et al., 2004; Gómez et al., 2011; Sanchez-Avila et al., 2012). Nevertheless, few studies were focused in marine sediments (Diez and Bayona, 2009; León et al., 2020; Sanchez-Avila et al., 2013; White et al., 2015), and, as far as we know, this is the first study including the analysis of these three families of contaminants in both matrices, seawater and sediments.

Presence of these substances in the marine environment is mainly caused by discharges of wastewater effluents, river flows, urban runoff following rain episodes, atmospheric deposition and degradation of plastics (Sanchez-Avila et al., 2012). Although these compounds are diluted in the open seawaters, their continuous input, and persistence causes that some of them have been detected in open seas and coastal areas (Yamashita et al., 2004). They can end up in the sediments by different mechanisms like the association with humic acids and adsorption onto particles (Paluselli et al., 2018b) acting as a reservoir and source of these contaminants through resuspension (Liu et al., 2014). Thereby, the high content of TBT is one reason why many sediments do not reach “Good Environmental Status” according to the MSFD (Eklund and Watermann, 2018), despite the prohibition of TBT since 1989 for use on leisure boats shorter than 25 m and all ships since 2008. This compound is still detected in water, biota, and sediments (with a half-life ranging from 0.9 to 15 years) specially in harbours (Thomaidis et al., 2007). Therefore, the monitoring of sediments is very helpful to assess the pollution status of these families of contaminants and to evaluate their potential environmental risks (Zhang et al., 2013).

For all these reasons, PFAS, OTCs and PAEs are included in the EU Water Framework Directive (WFD) 2013/39/EU as priority substances (WFD, 2013). The same approach with these toxic substances has been followed by the Marine Strategy Framework Directive (MSFD, 2008), tackling pollution in the marine environment. Also Perfluoro - 1 - octanesulfonate (PFOS) and its salts have been listed under Annex B (restricted use) of the Stockholm Convention in 2009 (The-Conference-of-the-Parties, 2010; Wang et al., 2009) and included in WFD. The recent “Chemicals Strategy for Sustainability Towards a Toxic-Free Environment” of the European Commission (European-Commission, 2020) highlights per- and polyfluoroalkyl substances (PFAS), and proposes a comprehensive set of actions to address the use of and contamination with PFAS taking into account their environmental impact.

This work aims to characterize the distribution of some toxic and hazardous substances, used as plastic additives among other uses, in seawater and marine sediments of two coastal areas located in the Spanish Atlantic and Mediterranean coasts. The North Atlantic area has high industrial and port activities (Ría de Vigo) and the Mediterranean one is subjected to high touristic and agricultural activities (Mar Menor lagoon, Western Mediterranean). The geographic and oceanographic characteristics of these areas could lead to an accumulation of certain contaminants within the inner part of the estuary strongly affected by continental inputs. Two sampling campaigns were carried out (spring and autumn) to characterize the seasonal variability of the different contaminants in each area. This is the first time that PFAS, OTCs and PAEs compounds are measured in seawater and sediments in these areas. Results obtained in both locations were compared, and finally, the whole data were used to estimate the ecological risk in seawater and sediments. Additionally, the identification of common sources and similar distribution patterns were evaluated using statistical analysis.

Therefore, the data obtained in this work are of great interest to identify priority substances for further assessment and contribute to

the EU's Strategy for Plastics in the Circular Economy in the substitution of hazardous substances with safer alternatives (European-Chemicals-Agency, 2016). Also, these results could be very useful in the Marine Strategy Framework Directive implementation.

2. Materials and methods

2.1. Materials and reagents

PFAS group: Individual standards of sodium perfluoro-1-octanesulfonate (PFOS), perfluoro-n-octanoic acid (PFOA), N-methylperfluorooctanesulfonamide (N-MeFOSA), N-ethylperfluorooctanesulfonamide (N-EtFOSA), 50 $\mu\text{g mL}^{-1}$ in methanol and Per-fluoro-1-octanesulfonamide (PFOSA) 50 $\mu\text{g mL}^{-1}$ in isopropanol were supplied by Wellington Laboratories (Canada). Isotopically labelled standards from Wellington Laboratories were used as surrogates: N-ethyl-d5perfluorooctanesulfonamide (d-N-EtFOSA-M) to correct N-EtFOSA and N-MeFOSA, sodium perfluoro-1-[1,2,3,4-¹³C₄]-octanesulfonate (MPFOS) and perfluoro-n-[1,2,3,4-¹³C₄]-octanoic acid (MPFOA) 50 $\mu\text{g mL}^{-1}$ in methanol; and perfluoro-1-[¹³C₈]octanesulfonamide 50 $\mu\text{g mL}^{-1}$ in isopropanol. Stock standards were stored at $-18\text{ }^{\circ}\text{C}$. Working standards (individuals and mixtures) were prepared from stock solutions by dilution in a mixture methanol:water (75:25) (working standard surrogate mix 50 $\mu\text{g L}^{-1}$), and stored refrigerated ($4\text{ }^{\circ}\text{C}$). Diluted standards were freshly prepared every two months to ensure the stability of standards. For water extraction 1-Octanol Chromasolv® (grade HPLC 99%) was from Sigma-Aldrich (Germany), and for sediment extraction methanol SpS was from Romil (UK). Supelclean™ ENVI-Carb™ SPE Bulk Packing used for dispersive solid-phase extraction (DSPE) clean-up was from Supelco (USA). HPLC mobile phases were methanol LC-MS grade from Fisher Chemical (UK) and water purified with a Direct 5 Milli Q system (Millipore, USA). Ammonium acetate was from Sigma-Aldrich.

OTCs group: Monobutyltin (MBT) trichloride, dibutyltin (DBT) dichloride, tributyltin (TBT) chloride, monophenyltin (MPHT) trichloride, diphenyltin (DPHT) dichloride and triphenyltin (TPHT) chloride were obtained from Sigma-Aldrich. Stock standard solutions of OTCs (1000 mg L^{-1}) were prepared in methanol. Tetrabutyltin (TeBT) was used as internal standard (Sigma-Aldrich). MBT-d₉, DBT-d₁₈ and TBT-d₂₇ (Dr Ehrenstorfer, Germany) were used as surrogate standards (each compound was corrected by its deuterated isotope) in sediment analysis (30 μL of 1 $\mu\text{g mL}^{-1}$ in methanol is added).

Sodium tetrapropylborate (NaBPr₄) was obtained from ABCR GmbH & Co (Karlsruhe, Germany). A fresh NaBPr₄ solution of 1% (w/v) was prepared daily in 2% NaOH solution (w/v) (Panreac, Barcelona, Spain). A HOAc/NaOAc buffer of pH 5 was prepared by adding an appropriate amount of glacial acetic acid (99.99%) to a 0.2 M solution of sodium acetate trace Select for trace analysis (both from Sigma-Aldrich) in milli-Q water. SPME fibers of 65 μm polydimethylsiloxane divinylbenzene (PDMS/DVB) were supplied by Supelco. For sediment analysis, isooctane (Panreac) (UV-PR-HPLC) PAI-ACS and octadecyl functionalized silica Supelclean-Envi18 Supelco (for the dispersion) were used.

PAEs group: A stock standard solution of phthalates mixture (dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DBP), butylbenzylphthalate (BBP), Di(2-ethylhexyl)phthalate (DEHP) and di-n-octylphthalate (DOP)) containing 2000 mg L^{-1} in methanol from Supelco was used to prepare calibration and working solutions. The internal standard, Benzyl Benzoate (5000 mg L^{-1}) was purchased from Restek Corporation (Bellefonte, PA; USA). For ultrasonic-assisted extraction (UAE), Methanol SpS from Romil was used.

2.2. Study areas and sampling campaigns

Mar Menor is a hypersaline (42–47 PSU, Practical Salinity Units) coastal lagoon, with a mean depth of 4.5 m and a maximum depth of 7 m. This lagoon is affected by higher seasonal fluctuations of

temperature and salinity than those detected in the Mediterranean Sea (Perez-Ruzafa et al., 2005). Ría de Vigo is affected by an intense outflow of nutrients and a positive estuarine circulation (Álvarez-Salgado et al., 2000). Their surroundings are highly urbanized, with a total population of ~428,000 inhabitants. The urban pressure is especially important at the central zone of the south seashore, where the city of Vigo is placed (~295,000 inhabitants).

The sampling campaigns were carried out in spring and autumn of 2015 (sampling points showed in Fig. 1), considering 6 sampling points in Ría de Vigo: RV1-RV5 and RV6 outside of the Ría close to Illas Cies (part of the Atlantic Islands of Galicia National Park), and 6 in Mar Menor: MM1-MM5 and MM8 outside of the lagoon in spring. Some additional sampling points were included in autumn to improve the spatial characterization in the lagoon and to get two external samples in both sampling areas (Atlantic and Mediterranean areas) as a consequence of the heterogeneity found in the first campaign (RV7 outside the estuary, MM6 and MM7 in the lagoon and MM9 outside the lagoon). Ría de Vigo (RV sampling points) were distributed along the estuary from the inner part (RV1) with the highest influence of several river discharges (Fig. 1) to the external estuary (RV5) with the highest dilution capacity of the system. RV4 and RV5 were close to the main urban-industrial wastewater treatment plant outfall. RV2 and RV3 were exposed to urban, aquaculture and navigation activities in a narrow area of this estuary. On the other hand, MM1, MM2 and particularly MM7 were subjected to the higher Mediterranean influence than the inner samples, and were close to the most important urban nuclei, ports and navigation channels. MM6 and particularly MM3 were in the influence area of El Albuñón watercourse discharge area, which was composed by groundwater.

Seawater samples were collected using a glass pitcher and stored in 1 L amber glass bottles at $10\text{ }^{\circ}\text{C}$ until arrival at the laboratory, where they were stored at $-20\text{ }^{\circ}\text{C}$ until further analysis. In Mar Menor area, one sample between 0 and 20 cm depth (superficial) was collected at each point. In Ría de Vigo two samples were collected at each point: superficial (0–20 cm) (S samples in the figures) and depth water samples (D samples in the figures) (5 m above the bottom). Sediment samples in Ría de Vigo were collected by oceanographic vessel "José María Navaz" using a box-corer, whereas in Mar Menor a Van Veen drag was launched from a pneumatic boat ("Posidonia Segundo"). About 5 kg of superficial sediments were collected in each sampling point, pooling samples obtained from 5 to 6 drags to get a representative sample and mass enough for all required analysis. Samples were lyophilized and freeze stored ($-20\text{ }^{\circ}\text{C}$) until analysis.

2.3. Water and sediment characterization

Temperature, pH, conductivity and dissolved oxygen of seawater were determined in situ using a portable multiparametric meter (WTW, model Multi 340i/SET*). The temperature ranged from $12\text{ }^{\circ}\text{C}$ to $16\text{ }^{\circ}\text{C}$ in Ría de Vigo, and from $16\text{ }^{\circ}\text{C}$ to $22\text{ }^{\circ}\text{C}$ and from $22.1\text{ }^{\circ}\text{C}$ to $24.1\text{ }^{\circ}\text{C}$ in Mar Menor in spring and autumn, respectively.

The total organic carbon (TOC) and the fine fraction were measured in sediment samples using a Perkin Elmer Series II CHNS/O Analyzer 2400. TOC varied from 2.2 to 11.6% in Ría de Vigo and from 0.7 to 17.5% in the Mar Menor lagoon. The fine fraction was quantified by wet sieving of the total fraction through a 0.063 mm mesh (values ranging from 1.0% to 89.7% and from 13.8% to 97.0%, for the Ría de Vigo and Mar Menor sediments respectively).

2.4. Chemical analysis

Following, the analysis methods used for PFAS, OTCs, and PAEs are described here in brief and detailed in the supplementary information.

PFAS (PFOA, PFOS, PFOSA, N-MeFOSA, N-EtFOSA) in seawater samples (35 mL of the sample) were extracted by vortex assisted liquid-liquid microextraction (VALLME) with octanol (100 μL) and determined

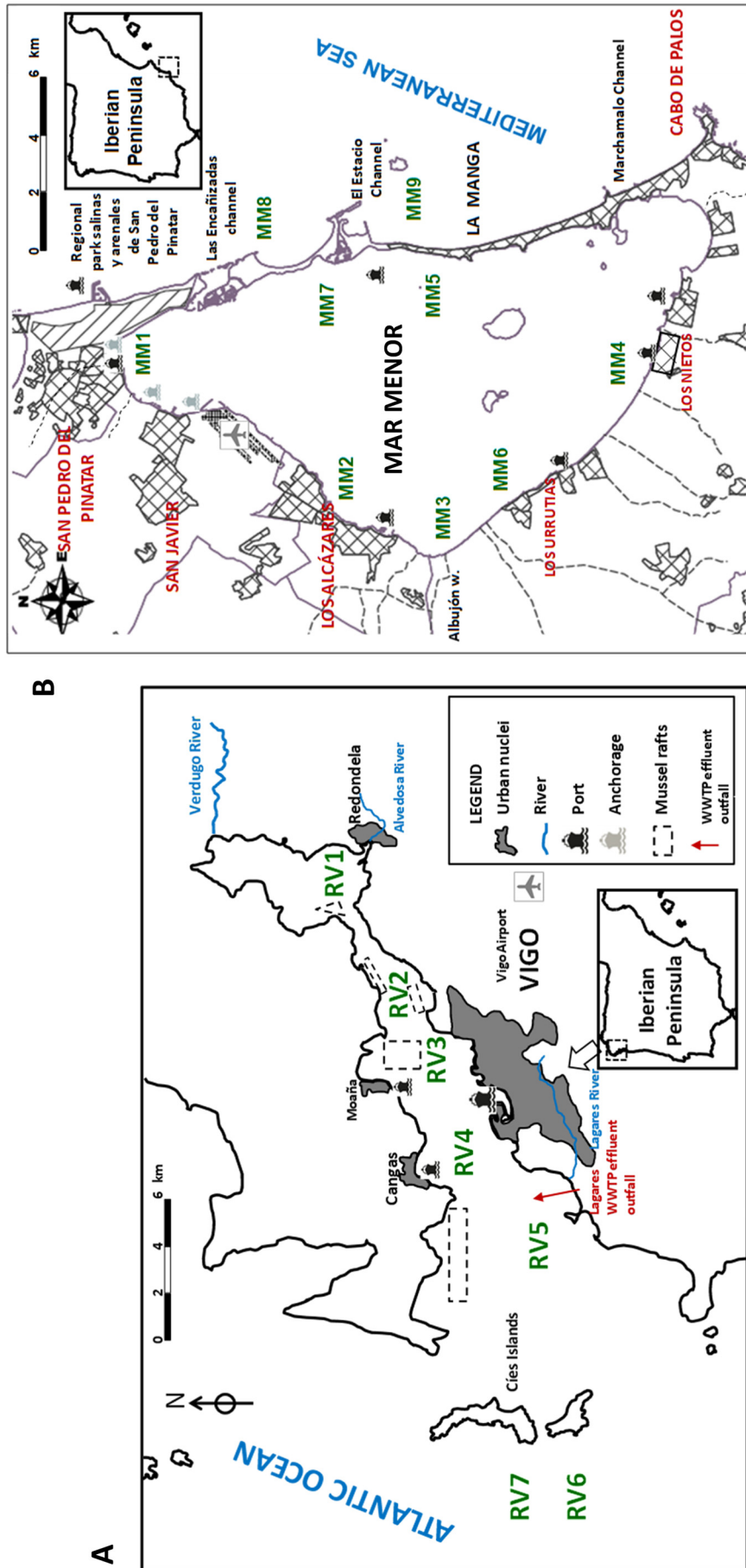


Fig. 1. Map of the studied areas indicating the location of the sampling points in each area: (A) Ria de Vigo and (B) Mar Menor.

Table 1

Statistical parameters of main contaminant groups and matrix properties in seawater from Mar Menor and Ría de Vigo. Mean values included into brackets were calculated considering only the inner point of Ría de Vigo and Mar Menor.

Sampling area	Season		Mean	S.D.	Minimum	Maximum	Median	>LOQ (%)	N
Mar Menor	Spring	Depth_(m)	3.27	0.74	0.90	5.90	2.80		6
		Temp_(°C)	19.90	0.67	16.70	21.30	20.36		6
		SolvO ₂ (mg L ⁻¹)	10.85	0.33	10.30	12.30	10.45		6
		Salinity	43.42	1.22	37.40	45.10	44.50		6
		Phthalates (ng L ⁻¹)	98 (96)	194	60	560	100.	16.7	6
		OTCs (ng L ⁻¹)	11.1 (11.4)	3.4	7.1	16.2	10.5	100	6
	Autumn	PFAS (ng L ⁻¹)	1.1 (3.2)	1.8	b.q.l.	5.7	2.2	83.3	6
		Depth_(m)	5.28	1.32	1.40	13.70	3.20		9
		Temp_(°C)	23.07	0.23	22.10	24.10	23.00		9
		SolvO ₂ (mg L ⁻¹)	7.59	0.13	7.00	8.20	7.55		9
		Salinity	43.69	1.28	36.90	46.00	45.60		9
		Phthalates (ng L ⁻¹)	b.q.l.	410	b.q.l.	1270	b.q.l.	11.1	9
		OTCs (ng L ⁻¹)	6.5 (6.2)	1.4	4.9	9.3	6.2	100	9
		PFAS (ng L ⁻¹)	1.5 (1.8)	0.5	b.q.l.	3.0	1.7	77.8	9
Ría de Vigo	Spring	Depth_(m)	18.80	8.67	0.15	93.00	0.15		11
		Temp_(°C)		11
		SolvO ₂ (mg L ⁻¹)		11
		Salinity		11
		Phthalates (ng L ⁻¹)	87 (100)	342	b.q.l.	1280	560	54.5	11
		OTCs (ng L ⁻¹)	2.7 (1.4)	2	b.q.l.	7.7	2.8	72.7	11
	Autumn	PFAS (ng L ⁻¹)	b.q.l.	0.5	b.q.l.	2.5	b.q.l.	36.4	11
		Depth_(m)	22.81	9.25	0.15	92.00	0.15		13
		Temp_(°C)		13
		SolvO ₂ (mg L ⁻¹)		13
		Salinity		13
		Phthalates (ng L ⁻¹)	b.q.l.	–	b.q.l.	b.q.l.	b.q.l.	0	13
		OTCs (ng L ⁻¹)	8.6 (8.6)	5.6	3.3	25.4	7.8	100	13
		PFAS (ng L ⁻¹)	b.q.l.	–	b.q.l.	1.6	b.q.l.	7.7	13

b.q.l.: below quantitation limit.

using LC-LTQ-Orbitrap-HRMS (Concha-Graña et al., 2018). PFAS were extracted from sediments (1 g) by UAE with methanol (8 + 5 mL), cleaned up by dispersive SPE with active carbon, concentrated, and then determined by LC-LTQ-Orbitrap-HRMS in full scan acquisition mode (Concha-Graña et al., 2017). For both matrices quantification

was performed using matrix-matched calibration and using the isotopically labelled PFAS as surrogates.

Organotin compounds (MBT, DBT, TBT, MPhT, DPhT and TPhT) in seawater samples were extracted from 10 mL of the sample by HS-SPME and in situ derivatization using NaBPr₄. Then, they were

Table 2

Statistical parameters of main contaminant groups and matrix properties in sediment from Mar Menor and Ría de Vigo. Mean values included into brackets were calculated considering only the inner point of Ría de Vigo and Mar Menor.

Sampling area	Season		Mean	S.D.	Minimum	Maximum	Median	>LOQ (%)	N
Mar Menor	Spring	Depth (m)	3.27	0.74	0.90	5.90	2.80		6
		Eh (mV)	−91.83	67.81	−314.00	120.00	−106.00		6
		Fine fraction (%)	43.22	16.28	0.93	89.66	40.76		6
		TOC (%)	7.00	2.86	1.42	17.52	3.40		6
		Phthalates (ng g ⁻¹)	1000 (225)	1361	72	3481	332.5	100	6
		OTCs (ng g ⁻¹)	12.1 (16.7)	19.4	b.q.l.	47.1	7.2	66.7	6
		PFAS (ng g ⁻¹)	0.12 (0.22)	0.1	b.q.l.	0.3	b.q.l.	83.3	6
	Autumn	Depth (m)	5.28	1.32	1.40	13.70	3.20		9
		Eh (mV)	−176.56	56.69	−398.00	120.00	−242.00		9
		Fine fraction (%)	41.20	12.26	0.56	89.63	39.80		9
		TOC (%)	4.29	1.36	0.79	11.75	2.11		9
		Phthalates (ng g ⁻¹)	458 (1141)	448	b.q.l.	1329	268	77.8	9
		OTCs (ng g ⁻¹)	11.5 (33)	41.5	b.q.l.	79.6	b.q.l.	33.3	9
		PFAS (ng g ⁻¹)	0.1 (0.04)	0.1	b.q.l.	0.4	0.1	55.6	9
Ría de Vigo	Spring	Depth (m)	35.32	12.54	6.00	93.00	28.50		6
		Eh (mV)		6
		Fine fraction (%)	88.59	4.51	67.22	97.23	92.58		6
		TOC (%)	8.42	1.07	3.41	10.85	9.03		6
		Phthalates (ng g ⁻¹)	1078 (1634)	568	80	1735	1082	100	6
		OTCs (ng g ⁻¹)	38.5 (24.7)	37.2	15.3	112.8	21.8	100	6
		PFAS (ng g ⁻¹)	b.q.l.	–	b.q.l.	b.q.l.	b.q.l.	0	6
	Autumn	Depth (m)	43.00	13.10	5.50	92.00	37.00		7
		Eh (mV)		7
		Fine fraction (%)	74.07	11.50	13.78	97.08	87.66		7
		TOC (%)	7.37	1.30	2.24	11.57	8.11		7
		Phthalates	1221 (1138)	649	178	2043	1375	100	7
		OTCs	20.42 (24.9)	12.6	b.q.l.	37.6	15.9	85.7	7
		PFAS	0.03 (0.07)	–	b.q.l.	0.1	b.q.l.	0	7

b.q.l.: below quantitation limit.

determined by GC–QqQ–MS/MS operating in selected reaction monitoring (SRM) detection mode (Moscoso-Pérez et al., 2015). OTCs were extracted from sediments (0.5 g) by MSPD–UAE, derivatized and finally determined by PTV–GC–QqQ–MS/MS operating in SRM detection mode (Munategui-Lorenzo et al., 2019).

Levels of phthalates (DMP, DEP, DBP, BBP, DOP and DEHP) in seawater samples (10 mL) were obtained by HS–SPME (with PDMS/DVB fibre) coupled to GC–MS detection in SIM mode acquisition (V Fernández-González et al., 2017). Sediments were analysed for phthalates by UAE with methanol followed by HS–SPME–GC–MS (V. Fernández-González et al., 2017).

The MQLs, accuracy and uncertainty of the compounds in each matrix were included in Table S1 of electronic supplementary information, together with the log K_{ow} values.

Environmental sediment–water partitioning coefficients ($K_d = C_s/C_w$, where C_s is the concentration in sediment (ng kg^{-1}) and C_w is the concentration in water (ng L^{-1})) were experimentally estimated for the different analytes and contaminant groups when they were found in both matrices. In this sense it is necessary to consider that there is not sorption equilibrium in these systems due to significant temporary variations in water concentrations.

2.5. Statistical analysis

Classical parametric descriptors were calculated using SPSS 15.0 for Windows (SPSS Inc. Chicago, IL, USA) (see Tables 1 and 2). The covariance between the different variables considered in this study was assessed using a linear correlation (Pearson). A minimum significance level of 95% was applied for all analyses. Multivariate factorial analysis (Principal Component Analysis, PCA) was applied using Varimax rotation to identify common pollution sources and distribution patterns.

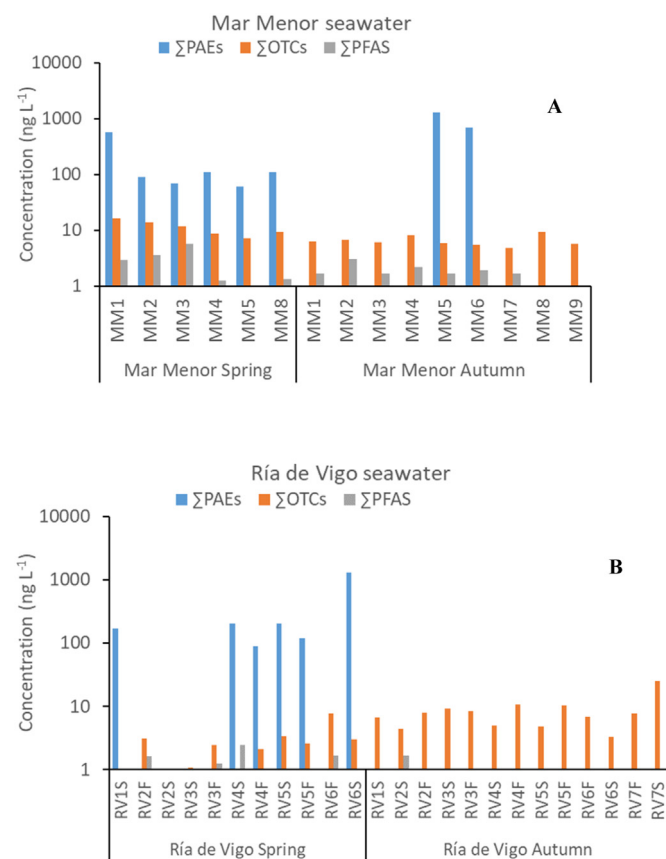


Fig. 2. Global representation of total concentrations of each family of additives studied in both areas, Mar Menor (A) and Ría de Vigo (B). The abscissa axis is expressed in the logarithmic scale (base 10).

2.6. Risk assessment

Ecological Risk Assessment (ERA) was estimated for the three families of pollutants to determine the possibility of negative effects, caused by the presence of these compounds on these marine ecosystems. The procedure to evaluate the ERA is based on the calculation of the risk quotient factor (RQ) in waters and sediments. RQ is defined as the ratio of measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC) ($RQ = MEC/PNEC$) (Palma et al., 2014). An average risk quotient was calculated considering a general scenario (RQ_m), using the geometric mean of the concentration of all the samples for each area in both sampling campaigns to determine the MEC. For concentrations lower than method quantitation limit (MQL), the half of its MQL was taking into account, according to the Directive 2009/90/EC (EC, 2009). The maximum detected concentrations were used for the worst-case scenario (RQ_{ex}). The RQ value was classified into 3 levels to assess the potential ecological risk: low ($RQ < 0.1$), moderate ($0.1 \leq RQ < 1$) or high risk ($RQ \geq 1$) (Palma et al., 2014).

The PNEC values calculated by Mhadhbi et al., were used for the estimation of risk quotient for PFOS and PFOA in seawater, calculated taking into account the effect at three different trophic levels (one microalga (*Isochrysis galbana*), a primary consumer (*Paracentrotus lividus*) and two secondary consumers (*Siriella armata* and *Psetta maxima*): $1.1 \mu\text{g L}^{-1}$ for PFOS and $119 \mu\text{g L}^{-1}$ PFOA, (Mhadhbi et al., 2012). For sediments, we use the $PNEC_{sed}$ estimated by the equilibrium partitioning method by EPA in 2004 ($6.7 \mu\text{g kg}^{-1}$ ww) to calculate the risk quotient of PFOS, since there is no toxicity data for sediment organisms (Brooke et al., 2004).

The PNEC values selected to calculate the risk quotient for organotin compounds in water and sediments were the PNEC values derived by INERIS, where the PNEC value of water is determined by using the EQS values of Directive 2008/105/EC, whereas the PNEC value for sediment is determined using the equilibrium partitioning method (INERIS, 2008).

Regarding PAEs, for DEHP, DBP and BBP PNEC values used were the published by the OSPAR Commission (OSPAR, 2006), and PNEC values for DMP and DEP were obtained from the Danish Environmental protection agency (DHI et al., 2014). In all cases the PNEC values are obtained considering the toxicity data of several species of the three trophic levels. The PNEC values in sediments reported in the previously cited references, were derived from the PNEC calculated for seawater, using the equilibrium partitioning method.

3. Results and discussion

Tables 1 and 2 show some relevant statistical parameters of the studied compounds in seawaters and sediments considering all sampling points (and considering only the inner point of Ría de Vigo and Mar Menor in parenthesis) of both areas. Average values for each compound were determined by assigning a value of half of the MQL for those samples below the quantitation limit according to 2000/60/CE Directive. Those compounds with average values below their MQL were not considered in the totals (sum of compounds of each family). Significant differences between seasons and areas were not observed due to the high spatial variability of concentrations found in both matrices which should be the consequence of many simultaneous and seasonal dependent sources in both areas.

In a general overview, comparing the total levels of each family of studied compounds is notorious that phthalates were present in seawaters at a concentration between one and two orders of magnitude higher than OTCs and PFAS (Fig. 2 A and B). It could be established that the main contributors (among those studied) to these areas contamination were the phthalates. Also, for sediments, the concentration of phthalates was much higher than concentrations of OTCs and PFAS.

In an aquatic system, the residence time of a pollutant and its distribution between water, sediments, and biota depends on its capacity to

binding to suspended particles and accumulate in sediments (Delle Site, 2001). This fact established the bioavailability of each compound to different species. In marine monitoring, spot sampling of water will offer punctual information about sources and pollutant distribution in each area. However, sediments will give an integrated view for longer periods for hydrophobic contaminants, being the distribution of contaminants influenced, not only by the distance to sources, but also by the predominant hydrodynamics and the sediment properties. For this reason, it is important consider the contamination of not only the aqueous phase (as established in the marine monitoring protocols), but also the sediments.

3.1. PFAS occurrence and distribution

3.1.1. Seawater

In seawater, PFOA was below the MQL ($<12.6 \text{ ng L}^{-1}$) in all samples of both areas, whereas for PFOS the average values were below MQL (0.66 ng L^{-1}) for Ría de Vigo and 1.34 ng L^{-1} for Mar Menor.

Seasonal differences were observed in both locations regarding not only the diversity of PFAS detected (higher in the spring period) but also the average amounts of PFAS. Mar Menor presented higher levels of PFAS than Ría de Vigo (where the average of total PFAS was below MQL in both sampling campaigns) (Table 1). All samples were below the MAC value established by the WFD, but the average concentration of PFAS in Mar Menor (1.6 ng L^{-1}) was higher than the annual average-Environmental quality standard of the directive (AA-EQS) value of the directive (0.13 ng L^{-1}) (Fig. 3).

In 3 samples from Mar Menor, the values of PFAS detected were below the quantitation limit (Fig. 3A), two of them corresponding to the external areas (MM8 and MM9) in autumn, possibly due to the highest dilution of these areas. PFOS was the most frequently detected PFAS, whereas PFOA and PFOSA were not detected in any sample. N-MeFOSA was found mainly in Mar Menor spring samples, and also N-EtFOSA but only in one sample. These compounds are considered insoluble in water, and for this reason, were scarcely found in water samples, and their presence was only reported in the literature at very low levels (pg L^{-1}) in the North Sea (Xie et al., 2013). N-MeFOSA is a precursor of PFOSA, and this a precursor of PFOS (Mejía Avedaño and Liu, 2015). Thus, the presence of N-MeFOSA can be relevant because it can lead to future PFOS presence. Sample MM3 presented the higher levels of PFAS (spring), including the presence of N-EtFOSA, an insecticide (sulfluramid), typically used for cockroach and ant control that could reach the area through submarine pipelines or surface runoff. This point is located in the influence area of El Albuji3n watercourse, the main collector of the Campo de Cartagena drainage basin, an area characterized by intensive agriculture and treated wastewater effluents. Continuous discharges were produced through this watercourse till March 2014 when the use of this effluent for agriculture irrigation began.

In Ría de Vigo area 19 samples were below the quantitation limit of PFAS. Sample RV2 presented a similar level of PFOS in both sampling campaigns (depth sample in spring, and surface sample in autumn) (Fig. 3B). This sample RV2 is located near to a fiberglass shipyard that could be the source of PFOS in this point. PFOA and PFOSA have not been detected in any of the analysed samples above their quantitation limits. N-MeFOSA and N-EtFOSA were detected in samples RV3D and RV4S respectively. The presence of N-MeFOSA could be justified by the WWTP of Vigo outfall which takes place in the central area of this estuary containing industrial and urban residues.

The values encountered in this work ($<12.6 \text{ ng L}^{-1}$ for PFOA, and $<0.66 \text{ ng L}^{-1}$ and 1.60 ng L^{-1} for PFOS in Ría de Vigo and Mar Menor respectively) were similar or lower than those reported in the literature at Cantabrian Sea coast ports (G3mez et al., 2011) or in Guanabara Bay (Quinete et al., 2009), but lower than those reported in areas subjected to higher urban and/or industrial pressures (T. Wang et al., 2011; Wille et al., 2010) (see Table S2).

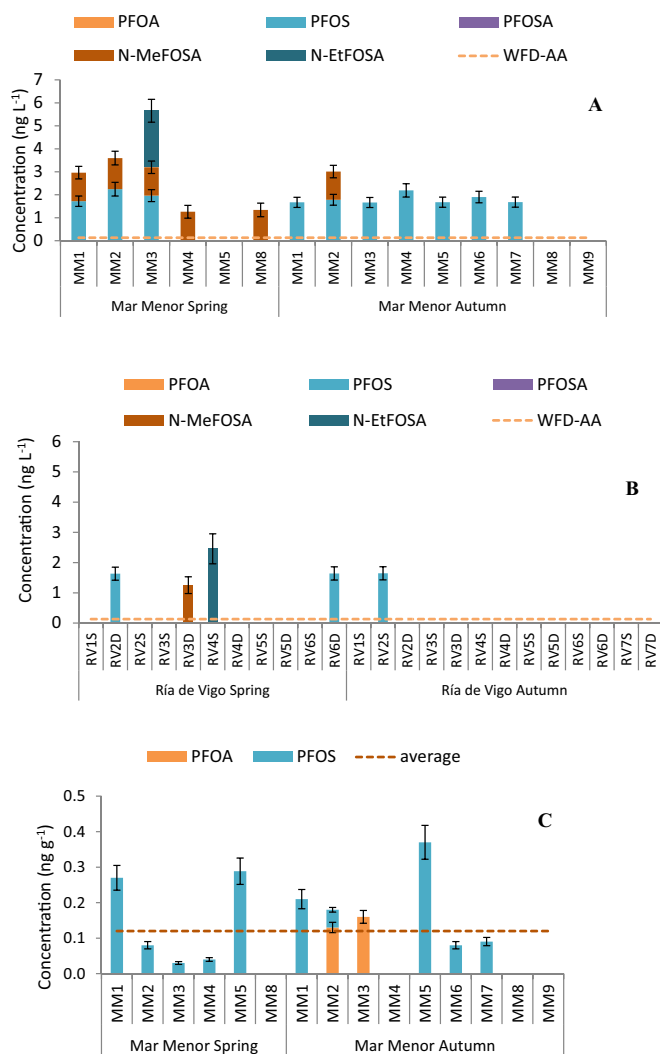


Fig. 3. PFAS results in seawater and sediments of both studied areas. Mar Menor seawater (A), Ría de Vigo seawater (B) and Mar Menor sediments (C). WFD-AA: Annual average limit established in the Water Framework Directive 2013/39/EU.

3.1.2. Sediments

Regarding sediment data (Table 2), also the average value for PFOA in the studied areas was below the MQL ($<0.10 \text{ ng g}^{-1}$ but 0.09 ng g^{-1} was quantified as average in Mar Menor spring samples). The average value for PFOS in Ría de Vigo was 0.05 ng g^{-1} considering only the inner samples. In Mar Menor the average value was 0.08 ng g^{-1} . Levels detected were similar than levels in similar areas (G3mez et al., 2011; Perra et al., 2013), and lower than levels of more industrial areas (Higgins et al., 2005; H. S. Wang et al., 2011; White et al., 2015). The values were also lower than those reported in sediments of Albufera wetland (Spain) (Lorenzo et al., 2019), probably due to the higher confinement and lower dilution of this coastal lagoon (Table S2).

In Mar Menor sediment samples, only PFOA (in two autumn samples) and PFOS were detected above their quantitation level. PFOSA was detected in two samples below its MQL (Fig. 3C). The concentration of PFOA or PFOS was low, no samples were detected above 0.4 ng g^{-1} . The highest concentrations were found in MM1 and MM5 both located in the northern basin of the lagoon. MM1 is close to Lo Pagan port and San Pedro del Pinatar and Santiago de la Ribera urban areas, and the levels of PFOS found in that location confirm the input of chemicals through urban run-offs, port and navigation activities. MM5 is near to El Estacio channel, a well-known deposition area with high navigation traffic. Regarding the external areas, MM8 and MM9 PFAS were not

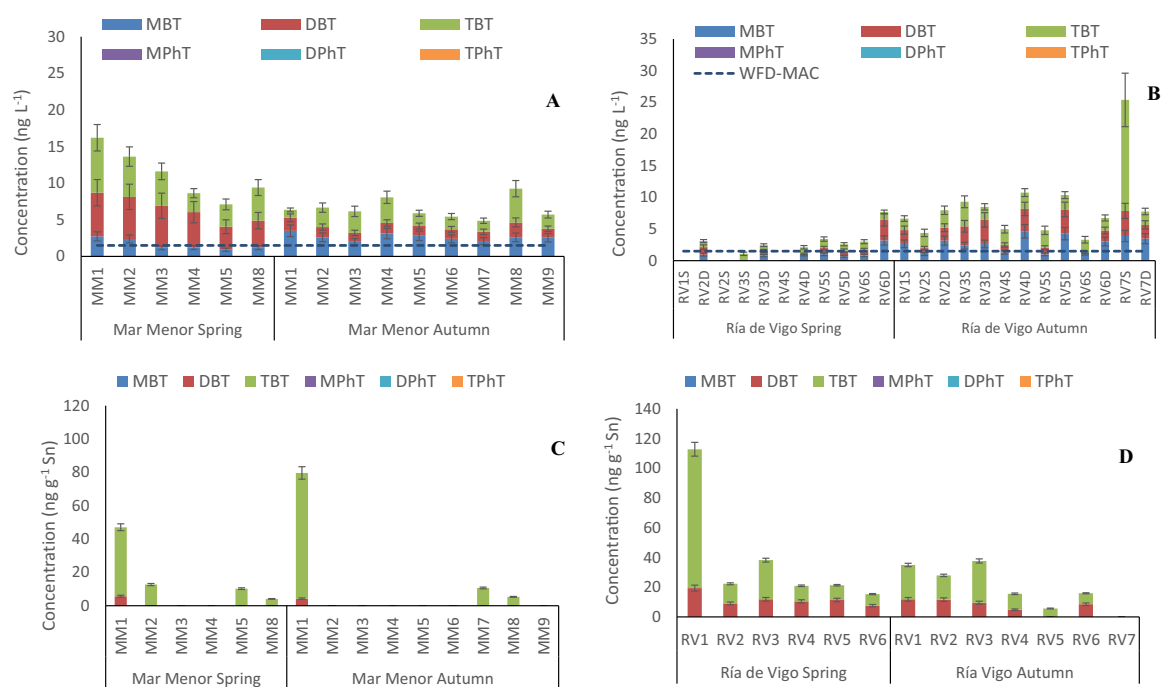


Fig. 4. OTCs results in seawater and sediments of both studied areas. Mar Menor seawater (A), Ría de Vigo seawater (B), Mar Menor sediments (C) and Ría de Vigo sediments (D). WFD-MAC: maximum admissible concentration established in the Water Framework Directive 2013/39/EU.

detected, confirming the dilution effect. The concentration of PFOS detected in both seasons is quite similar, confirming that the presence of PFOS in the area is not due to punctual contamination.

Regarding Ría de Vigo sediments, only PFOS in sample RV7 (autumn) was detected above the MQL (0.09 ng g^{-1}). This point is located in the outer point of the estuary, and there was not a clear source for PFOS level in this sample.

These compounds were found more frequently in the aqueous phase than sorbed to sediments, probably close to main sources, and the sorption to sediments depends on the sediment (organic content, granulometry, etc.) and seawater characteristics (ionic strength, temperature, etc.). PFOS K_d was experimentally estimated using Mar Menor samples data, obtaining an average value of $\log K_d = 1.62 \pm 0.34$. Although it is necessary to clarify this value corresponded to a non-equilibrium system due to the high temporary variability of seawater concentrations. This value is similar than the reported in South Korea estuaries ($\log K_d = 1.7 \pm 0.3$, for salinity between 14 and 29 PSU) (Hong et al., 2013) and lower than the reported in continental water areas like an aquatic system in the Netherlands ($\log K_d = 2.35 \pm 0.35$) (Kwadijk et al., 2010) or a China river ($\log K_d = 2.31 \pm 0.71$) (Lv et al., 2019), that is in agreement with the reported dependence of the partition coefficient with the ionic strength (Hong et al., 2013).

3.2. OTCs occurrence and distribution

3.2.1. Seawater

The phenylated compounds of Sn were not found in concentrations above the MQL (see Fig. 4 and Table S1) in any of the samples. In Mar Menor, values of MBT between 0.91 and 3.50 ng L^{-1} , DBT between 1.22 and 5.96 ng L^{-1} and TBT between 1.08 and 7.50 ng L^{-1} were found in the samples analysed (Fig. 4A). In the Vigo estuary, values are lower than found in Mar Menor, with some samples below MQL ($<0.47 \text{ ng L}^{-1}$ for MBT, $<0.74 \text{ ng L}^{-1}$ for DBT and $<0.76 \text{ ng L}^{-1}$ for TBT) and average values of 1.83 ng L^{-1} , 1.65 ng L^{-1} and 2.37 ng L^{-1} for MBT, DBT and TBT respectively (Fig. 4B). The highest value of TBT (17.5 ng L^{-1}) was found in the RV7 (autumn) sample. This point is located in the outer point of the estuary close to Illas Cies.

Higher concentrations were found in spring than in autumn for Mar Menor, nevertheless, for Ría de Vigo the highest values were found in autumn. This could be due to the increased land run-off in the month before the sampling time.

TBT, identified in the WFD as a priority hazardous substance with a maximum permissible concentration of 1.5 ng L^{-1} , was present in 92% of the total 39 samples analysed, being detected in 100% of Mar Menor samples and 88% of Ría de Vigo samples (Table 1).

In seawater, the levels of OTCs found in this study (Table 1) were similar to those detected in some similar locations (see Table S3) (Furdek et al., 2012; Segovia-Martínez et al., 2010), and lower than the detected in great maritime traffic ports (Chou and Lee, 2005; Thomaidis et al., 2007).

3.2.2. Sediments

In Mar Menor, phenylated compounds of Sn were not found in concentrations above the MQL (Table S1) in any of the samples.

Regarding butylated compounds, MBT was not found in concentrations above the MQL ($7.97 \text{ ng g}^{-1} \text{ Sn}$) in any of the samples, and DBT was only detected in two of them (one in spring $5.70 \text{ ng g}^{-1} \text{ Sn}$ and the other in autumn $4.25 \text{ ng g}^{-1} \text{ Sn}$). The compound with greater concentration and abundance in both campaigns was the TBT (values between 4.10 and $75.4 \text{ ng g}^{-1} \text{ Sn}$). The highest value was found in sample point MM1 in both the autumn and spring campaigns and it is also found in MM8 (in the outside of the lagoon), MM2 and MM5 of the spring campaign and MM7 of the autumn campaign (Fig. 4C).

MM1 station is located close to Lo Pagan port and an urban area, which would explain the level of TBT found at this point, since it was used for a long time as a PVC stabilizer, to prevent its thermal and light degradation, as well as an additive in antifouling paints for boats, preservatives for wood or as a fungicide. The same applies to samples MM8, MM5 and MM7, all of them close to marinas and/or the main navigation routes.

The values of OTCs found in these samples (Table 2) were, in general, lower than those found in the literature (Table S3), being, for example, the values 200 times higher in the port of Barcelona (Diez and Bayona, 2009) or port areas of the Basque Coast (North Spain) (German Rodriguez et al., 2010). The highest values reported (up to more than

500 times higher) corresponded to ports in different cities located along the Spanish Mediterranean coast, with intense maritime traffic and close to industrialized areas (Diez et al., 2002). As it was expected, the average concentrations of OTCs found in these semiconfined areas were higher than the recently reported in platform sediments (2.5 ng g⁻¹ in Mediterranean platform and <MQL in Atlantic platform) (León et al., 2020).

Although its use is banned since 2008, the degradation of TBT in sediments is much slower than in waters, where half-lives are estimated to be up to 10 years (Chen et al., 2019). In marine sediments, TBT degrades via debutylation, i.e. TBT-DBT-MBT-Inorganic tin. This TBT degradation process can be quantified by the calculation of the butyltin degradation index (BDI) where MBT, DBT and TBT refer to their total concentrations.

$$BDI = \frac{MBT + DBT}{TBT}$$

In Mar Menor samples, the samples where the BDI < 1 corresponding to the samples where the TBT levels are higher (MM1, MM5, MM7 and MM8), which indicate a “recent” input of TBT. This should be a consequence of the proximity of these sampling points to the main ports and navigation routes of this lagoon.

In Ría de Vigo (Fig. 4D), phenylated compounds of Sn and MBT were not found in concentrations above the limit of quantitation in any of the samples. Although the concentrations were not much higher than those found in the Mar Menor, DBT (4.86–19.4 ng g⁻¹ Sn) and TBT (5.65–93.4 ng g⁻¹ Sn) were found in all samples studied, except in RV7 during autumn, in which none of the organotin compounds studied has been detected. This area is subjected to more relevant port and navigation activities than Mar Menor lagoon, but it also has higher dilution capacity due to the water flow (river discharges and tides).

TBT showed the highest concentration (RV1 station in spring) and abundance (92% of the 13 samples analysed), in both campaigns. Although high values of this compound were also detected in point RV1 of the autumn campaign and point RV3 in both campaigns. The station RV1 is located in the inner part of the estuary, near the mouth of a river, so it may be affected by runoff and dilution capacity is lower than in the rest of the estuary. The station RV3 is close to highly industrialized areas (Vigo). In this area, in addition to the contribution due to the presence of the port, there are PVC industries. The DBT is a degradation product of TBT and also has its use in the PVC industry (Bolam et al., 2014). BDI values were below 1 only in RV1 and RV3, confirming the presence of recent inputs for TBT in these points.

As well as in the case of PFAS, DBT and TBT K_d were experimentally estimated in both locations (in Ría de Vigo depth water samples results were used for the calculation). Log K_d = 3.70 ± 0.35 for DBT and log K_d = 3.91 ± 0.31 for TBT were obtained in Ría de Vigo as average, whereas log K_d = 3.18 ± 0.28 for DBT and log K_d = 3.62 ± 0.63 for TBT were obtained as averages in Mar Menor, evidencing the preferential accumulation of these contaminants in sediments. A similar value was obtained for TBT in the Bowling basin in Glasgow (log K_d = 3.64) (Bangkedphol et al., 2009).

3.3. Phthalates occurrence and distribution

3.3.1. Seawater

The values of PAEs found in this study (Tables 1 and 2) were, in general, lower than those reported in the literature (Table S4). In seawater, almost all the samples analysed in this study were below the MQL (Tables 1 and S1), as it was observed in other areas. The method quantification limits varied between 60 ng L⁻¹ (DOP) and 2280 ng L⁻¹ (DBP) in this matrix, similar to those found in previous studies, due to the procedural blank problems typical for the analysis of these compounds. Although phthalates were found at high concentrations in sediments, very

low levels were found in seawater due to their hydrophobicity which favours the transfer to suspended materials and sediments.

In the spring campaign of Mar Menor, only DOP was detected at low concentrations (ranged 60–150 ng L⁻¹). This compound was also found in some samples of Ría de Vigo (RV1S, RV4 surface and bottom waters and RV5 surface and bottom) in the same sampling campaign (values between 90 and 200 ng L⁻¹). BBP in MM1 sample and DMP in Ría de Vigo were also found (410 and 1280 ng L⁻¹ respectively). DEHP was found in two samples of autumn in the Mar Menor MM5 (1270 ng L⁻¹) and MM6 (690 ng L⁻¹). The concentration in MM5 station was in the limit set by the WFD (1300 ng L⁻¹ annual average). In the autumn campaign of the Ría de Vigo, none of PAEs analysed was found above the MQL.

DOP was the PAEs more frequently found in the water samples (28%), although is the most hydrophobic compound of the PAEs analysed in this work, followed by DEHP (5%) and DMP and BBP (3%). Their occurrence in seawater was a consequence of the distance to the main sources, their fast degradation process (Liang et al., 2008) and their transfer to sediments favoured by sorption on particulate material. PAEs of lower molecular weight (LMW-PAEs: C₃–C₆) are used as essential components of some solvents, adhesives, waxes, pharmaceuticals, biocides and cosmetics, whereas PAEs of higher molecular weight (HMW-PAEs: C₇–C₁₃), as DOP, are used as plastic additives to improve the flexibility and handling of industrial materials (Paluselli et al., 2018a). Therefore, the presence of DOP in these samples could indicate contamination by plastic materials.

The levels of PAEs obtained in this work were similar than the reported in the literature (Table S4), for N coasts of Spain (Sanchez-Avila et al., 2013) or Eastern coast of Thailand (Malem et al., 2019).

3.3.2. Sediments

PAEs were detected in almost all samples collected, which indicates that sediment is a significant sink for PAEs as a consequence of their hydrophobicity. DEP, DEHP and DOP were the most detected of the targeted PAEs, being present in the 75% (DEP) and 71% (DEHP and DOP) of the total samples analysed. The average concentrations in the Mar Menor were 1.00 µg g⁻¹ and 0.46 µg g⁻¹ in spring and autumn, respectively, and in sediments from Ría de Vigo 1.08 µg g⁻¹ and 1.22 µg g⁻¹ in spring and autumn, respectively.

Regarding Mar Menor samples, PAEs were found in all samples (Table 2), except in MM3 and MM5 of the autumn campaign. Surprisingly, these two sampling points had the highest sum of the 6 PAEs of the spring campaign concentrations (ΣPAEs, only the sum of the values above of the MQL), with ΣPAEs values of 1.72 and 3.48 µg g⁻¹ respectively. Probably it should be a consequence of the faster degradation of PAEs in warmer periods (Wang et al., 2017). In fact, the PAEs values found in autumn in the Mar Menor were much lower than those in spring (see Fig. 5), probably as a consequence of their faster degradation during summer due to the highest temperatures (close to 30 °C), which was the optimal temperature for some bacterial consortium to degrade DBP (Wang et al., 2017).

DEP showed the highest concentration and occurrence in both campaigns, contributing, between 44 and 98% of the Σ6PAEs pollution in the spring campaign and between 57 and 100% in the autumn campaign. This phthalate is widely used in the cosmetic industry (for example in perfumes or as a base in detergents), and virtually all plastic objects. The highest concentration of DEP was found in MM5 during the spring campaign (1.84 µg g⁻¹), although a high value in the MM8 (0.91 µg g⁻¹) was also found. This sample is located outside of the Mar Menor Lagoon, but probably it was subjected to the influence of San Pedro del Pinatar WWTP outfall and port.

In the spring campaign, the DEHP was found in the analysed samples with a contribution percentage between 19% (MM5) and 85% (MM2), being the phthalate that most contributed in the Σ6PAEs together with DEP. DOP was found in all the samples, although its contribution percentage in the Σ6PAEs was very low (between 0.2 and 15%).

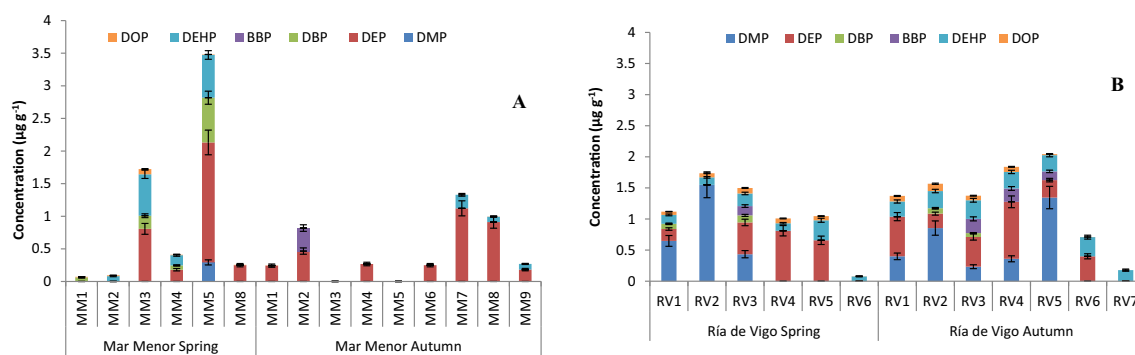


Fig. 5. PAEs results in sediments of both studied areas. Mar Menor sediments (A) and Ría de Vigo sediments (B).

However, in the autumn campaign, the greatest contribution was due to DEP (82.4%).

The total concentration of $\Sigma 6$ PAEs in Ría de Vigo sediment samples was quite similar to the Mar Menor ones, but more PAEs congeners were detected. The exceptions were the RV6 and RV7 samples (located in the oceanic zone outside of the estuary) in both campaigns, where DEHP was the only PAEs found at very low concentrations. The fine particle percentage and organic matter content were quite similar in all the sampling points, except in these RV6 and RV7 locations where both percentages were significantly lower. Since the PAEs are hydrophobic compounds and tend to be sorbed to by organic matter, these factors can affect the retention capability of the PAEs in sediments, together with the higher dilution in these sampling points sited in the external area of Ría de Vigo.

The sampling stations with the highest $\Sigma 6$ PAEs concentrations were RV2 and RV3 in spring. These concentrations were of the same order in autumn, but the greatest concentrations were found in RV4 and RV5 (1.84 and 2.04 $\mu\text{g g}^{-1}$, respectively).

In addition to urban, industrial and port activities, other possible sources of these additives in RV2 and RV3 were the mussel cultivation rafts, which are very abundant near these areas due to the relevant aquaculture activity that takes place in Ría de Vigo. The main structure of these platforms is made of wood, although the ropes, buoys and other components are made of plastic material.

The compounds found at higher concentrations were DEP and DMP, with maximum values of 0.91 $\mu\text{g g}^{-1}$ of DEP in RV4 (autumn campaign) and 1.55 $\mu\text{g g}^{-1}$ of DMP in RV2 (spring campaign).

The PAEs with the higher percentage of contribution to the $\Sigma 6$ PAEs in the spring campaign were DMP (29–89%), DBP (17–80%) and DEHP (7–96%). DOP appeared in all sampling stations of Ría de Vigo (Fig. 5), although with percentages of contribution relatively low between 4 and 8%.

In the autumn campaign, PAEs with higher contribution to $\Sigma 6$ PAEs were DMP between 17% (RV3) and 66% (RV5); DEP between 14 (RV5) and 50% (RV4) and DEHP between 13 (RV5) and 100% (RV7). DOP appears again in all samples, although with contributions between 0.3 and 7%.

The average concentrations of these compounds in sediments from Mar Menor lagoon and Ría de Vigo (Fig. 5 and Table S4) were lower than those found in Bohai and Yellow sea in China (Zhang et al., 2018) or Caspian Sea coast (Hassanzadeh et al., 2014), but comparable to the reported in areas similar than the studied like the Cantabric Sea ports and estuaries (Sanchez-Avila et al., 2013).

3.4. Correlation analysis: identification of distribution patterns

To identify the nature of the sorption of the studied compounds to the sediment, the correlation between the concentration of each compound with some physical-chemical parameters of the sediment samples was determined, as a percentage of particles <63 μm , percentage

of organic carbon and redox potential. Regarding PFAS and OTCs in Mar Menor, significant positive correlations ($r = 0.64$ and 0.68 respectively, $p < 0.05$) were observed in sediment samples with organic carbon considering both seasons, and only with fine fraction for PFAS ($r = 0.65$, $p < 0.05$). Attending to individual contaminants DBT ($r = 0.72$, $p < 0.01$), TBT ($r = 0.65$, $p < 0.05$) and PFOS (0.76 , $p < 0.01$) were positively correlated with TOC in this area, and PFOS showed also significant positive correlations with fine sediment fraction ($r = 0.66$, $p < 0.05$). An exponential diminution of PFOS content was observed ($y = 0.0497e^{-0.004x}$, $r^2 = 0.549$) for both campaigns Mar Menor samples when the redox potential increase from negative values to positive ones. That could indicate an increasing PFOS degradation as oxygen content increases. In Ría de Vigo sediments, OTCs were negatively correlated ($r = 0.68$, $p < 0.05$) with depth (mainly due to the contribution of DBT and TBT), showing the highest concentrations in the inner part of this estuary. However, no significant correlations were found for any of the contaminants groups with TOC or fine sediment fraction in this study area, except for DBP and DOP which showed negative correlations ($r = 0.69$ and 0.63 respectively, $p < 0.05$) with the fine fraction.

For Mar Menor seawaters, OTCs showed negative correlations with temperature ($r = 0.58$, $p < 0.05$) and salinity ($r = 0.72$, $p < 0.01$), and positive ones with dissolved oxygen. This relationship was probably due to the main ports and navigation routes in the northern areas of this lagoon, which are subjected to higher Mediterranean influence (lower temperature and salinity, and higher oxygen than the southern areas). Consequently, other factors should be predominant in the distribution of these contaminants such as the distance to the main pollution sources and the hydrodynamic conditions of each coastal system.

The study of correlations between families of compounds could help to identify common distribution patterns and contamination sources. Regarding seawater samples, no correlations were found between phthalates and PFAS or OTCs, whereas the Pearson test showed a statistically significant positive correlation ($r_{\text{obtained}} = 0.694 > r_{\text{tabulated}} = 0.497$, $p < 0.1$) between OTCs and PFAS in Mar Menor which could indicate that both families come from the similar pollution sources. One common source of both families could be plastics, but the no correlation with PAEs data should indicate other sources for PFAS and OTCs, probably ports and navigation. For Ría de Vigo there was not enough pair of data to perform the test. Considering sediments, only DBT and TBT were positively correlated in Ría de Vigo ($r = 0.79$, $p < 0.01$) and negatively for DMT and DEP concentrations ($r = 0.8$, $p < 0.01$) showing similar distribution patterns. However, different correlations were observed between individual contaminants in Mar Menor lagoon and for this reason, the factorial analysis was applied. The first factor (33.6% of variance) was characterized by high loadings of DBT, TBT, PFOS, fine fraction and TOC, showing the preferential accumulation of these contaminants in depositional areas with high organic carbon content. Factor 2 (31.7% of variance) was related to the influence of phthalates pollution, including positive contributions of DBP, DMP,

DEP and DEHP, but not for DOP and BBP which showed different distribution patterns. This factor should be related to specific pollution sources for PAEs, probably associated with urban and industrial wastewater discharges which are transported and disposed of preferably in depositional areas.

3.5. Ecological risk assessment

As it was previously mentioned, concentrations of PAEs in seawaters and sediments were higher than concentrations of PFAS and OTCs. Nevertheless, that does not necessary means that phthalates suppose a higher environmental risk. When the concentration of each family of compounds is related to the maximum admissible concentration established in WFD (Fig 6 A and B) revealed that organotin compounds were the main contributors to contamination in almost all sampling points.

To evaluate the contribution of each compound to the ecological risk of each area, the ecological risk assessment for each family was estimated as it was described in the Section 2.6.

Regarding PFAS, the risk quotient was only calculated for PFOS (Table 3), and the values obtained were very low (<0.1) in both locations and matrices (water and sediments). Considering the three risk levels, levels of PFOS in waters and sediments of these areas did not suppose a risk for the aquatic organisms. Nevertheless, taking into account the ability of PFAS to be bioaccumulated, and their occurrence in coastal areas, their potential effect on human health through the trophic chain should be evaluated. For this reason, it is important to monitor its presence in the marine environment, especially in Galicia, pointed out as one of the areas with the highest exposure to PFAS levels by a study about levels of PFAS in Spanish adults, being one of the sources of PFAS established in this work the seafood ingestion (Bartolome et al., 2017).

The risk quotient for the OTCs was only calculated for DBT, TBT and MBT (this only in seawater) (Table 3) because average MBT concentrations in sediments and average TPhT concentrations in seawaters and sediments were below the detection limit.

For seawater samples, low risk ($RQ < 0.1$) was found for MBT and DBT, however, high risk was found for TBT considering general (RQ_m) and extreme scenarios (RQ_{ex}) in both sampling areas (MM1 and RV7S samples).

Concerning sediments, high risk ($RQ \geq 1$) was found in Ría de Vigo for both MBT and TBT. In Mar Menor lagoon, when an extreme scenario was considered, a high risk was obtained for DBT in MM1 from spring campaign ($RQ_{ex} = 1.84$). TBT posed a high risk with values of $RQ_{ex} > 1$ in the same sample (MM1) from the autumn campaign.

Regarding PAEs, only DMP pose a low risk in seawaters of Ría de Vigo (Table 3), both, in a general scenario, and extreme conditions. Nevertheless, in Mar Menor seawater, low risk was obtained for DEHP and a medium risk for BBP considering the general scenario, but the medium risk was obtained for both compounds when the extreme scenario was

Table 3

RQ_m and RQ_{ex} values for PFOS OTCs and PAEs in Ría de Vigo and Mar Menor seawaters and sediments.

	PNEC	Ría de Vigo		Mar Menor lagoon		Risk
		RQ_m	RQ_{ex}	RQ_m	RQ_{ex}	
PFOS _w	1100 ng L ⁻¹	–	0.00150	0.00115	0.00199	Low risk
PFOS _{sed}	6.7 µg kg ⁻¹	–	0.013	0.015	0.055	Low risk
MBT _w	0.1 µg L ⁻¹	0.02	0.05	0.02	0.04	Low risk
DBT _w	0.2 µg L ⁻¹	0.01	0.02	0.01	0.03	Low risk
DBT _{sed}	3.09 µg kg ⁻¹	2.97	6.27	–	1.84	High risk
TBT _w	0.0002 µg L ⁻¹	11.9	87.6	16.5	37.5	High risk
TBT _{sed}	0.02 µg kg ⁻¹	979	4671	586	3770	High risk
DMP _w	19.2 µg L ⁻¹	0.03	0.07	–	–	Low risk
DEHP _w	6 µg L ⁻¹	–	–	0.06	0.21	Medium risk
DEHP _{sed}	20,000 µg kg ⁻¹	0.011	0.016	0.007	0.033	Low risk
BBP _w	0.75 µg L ⁻¹	–	–	0.14	0.547	Medium risk
BBP _{sed}	172 µg kg ⁻¹	0.578	1.331	0.473	2.052	Medium-high risk
DEP _{sed}	13.7 µg kg ⁻¹	29.9	66.7	33.1	50.1	High risk
DBP _{sed}	300 µg kg ⁻¹	0.158	0.377	0.299	2.287	Medium-high risk

considered, corresponding to MM5 autumn sample for DEHP and MM1 spring sample for BBP.

Concerning sediments, the RQ_m estimated in Ría de Vigo samples, revealed low risk due to DEHP, the medium risk for DBP (RV3 spring), and high risk for DEP (RV4 autumn campaign) considering the general and extreme scenarios. For BBP medium risk was obtained in the general scenario and high risk considering the extreme value (RV3 autumn). In Mar Menor, low risk was obtained for DEHP, but a medium risk for BBP and DBP and high risk for DEP were obtained in the general scenario. Considering the extreme conditions high risk was obtained for BBP (MM2 autumn), DEP (MM5 spring campaign) and DBP (also MM5 spring campaign). These results indicate that PAEs pose a higher environmental risk for the sediments than the seawater, and for this reason sediments should be taking into account when risk assessment was estimated, particularly for hydrophobic substances, not being enough to analyse spot seawater samples subjected to a great spatial and temporary variability.

Considering all the compounds, the Mar Menor MM1 point, located close to Lo Pagan port and San Pedro del Pinatar and Santiago de la Ribera urban areas seems to be subjected to a high environmental risk, affecting seawater (TBT and BBP) and sediments (TBT).

4. Conclusions

The occurrence of PFAS, OTCs and PAEs was confirmed for the first time in both studied areas. PFAS were detected at low concentrations, both in seawater (<MQL to about 3 ng L⁻¹), and sediments (<MQL to about 0.2 ng g⁻¹). Concentrations detected in seawater were below the MAC of WFD, but 33% of samples were above the AA of WFD, and for these reason, PFAS should be included in monitoring programs in these areas. Regarding OTCs in seawater, the concentration found

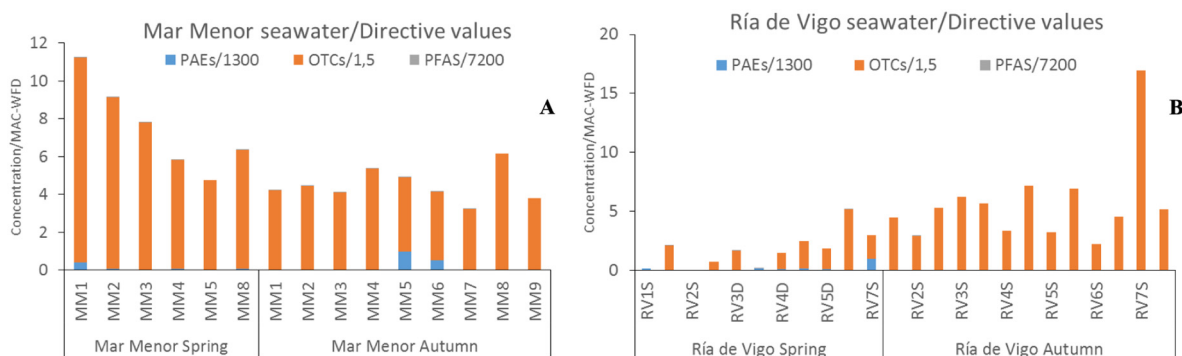


Fig. 6. Total concentrations of each family related to the WFD-MAC values (A: Mar Menor, B: Ría de Vigo). Contribution of each family to the environmental risk.

ranged between <MQL and about 20 ng L⁻¹, whereas for sediments ranged between <MQL and around 100 ng g⁻¹. PAEs were scarcely detected in seawater samples, but when detected, the concentrations were higher than those found for the other families (from <MQL to about 2000 ng L⁻¹), whereas in sediments were found in almost all samples (from <MQL to about 2000 ng g⁻¹). These results also evidenced the necessity to consider an integrative matrix (biota, sediment or passive samplers) for the environmental analysis of hydrophobic organic contaminants instead of spot seawater samples which show high spatial and temporary variability.

In general, the highest concentrations of all the studied compounds were found in Mar Menor seawaters, being here one of the points most affected by the presence of the three families analysed (MM5), a depositional area with high maritime traffic. The sediment sample in this point showed also high values of PAEs and PFAS. However, for PAEs and OTCs, the highest values for sediments were detected in Ría de Vigo, where it is located one of the most important ports in the North of Spain. In Mar Menor sediments, the distribution of PFOS and OTCs was mainly associated with depositional areas (high fine fraction) and high organic carbon content, but not for PAEs. However, no significant correlations with sediment properties were observed in Ría de Vigo, probably as a consequence of the predominant influence of distance to specific pollution sources for the different contaminants.

Low risk for aquatic organisms was obtained for PFAS in seawater and sediments of both areas, whereas for PAEs the risk was low or medium for seawaters, but a medium/high risk in sediments, being DEP the main contributor to risk. The higher contributors to the environmental compromise in both areas were OTCs, with high risk obtained for TBT in both matrices and DBT in sediment.

CRedit authorship contribution statement

Estefanía Concha-Graña: Methodology, Validation, Investigation, Formal analysis, Writing – original draft. **Carmen Moscoso-Pérez:** Methodology, Validation, Investigation, Formal analysis, Writing – original draft. **Verónica Fernández-González:** Methodology, Validation, Investigation, Formal analysis, Writing – original draft. **Purificación López-Mahía:** Conceptualization, Resources, Supervision. **Jesús Gago:** Conceptualization, Resources, Supervision. **Víctor M. León:** Project administration, Supervision, Writing – review & editing, Conceptualization. **Soledad Muniategui-Lorenzo:** Project administration, Supervision, Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.146450>.

References

- Álvarez-Salgado, X.A., Gago, J., Martín Míguez, B., Gilcoto, M., Pérez, F.F., 2000. Surface waters of the NW Iberian margin: upwelling on the shelf versus outwelling of upwelled waters from the Rías Baixas. *Estuar. Coast. Shelf Sci.* 51, 821–837.
- Bangedphol, S., Keenan, H.E., Davidson, C., Sakultantimetha, A., Songsasen, A., 2009. The partition behavior of tributyltin and prediction of environmental fate, persistence and toxicity in aquatic environments. *Chemosphere* 77, 1326–1332.
- Bartolome, M., Gallego-Pico, A., Cutanda, F., Huetos, O., Esteban, M., Perez-Gomez, B., Castano, A., Bioambient.es, 2017. Perfluorinated alkyl substances in Spanish adults: geographical distribution and determinants of exposure. *Sci. Total Environ.* 603–604, 352–360. <https://doi.org/10.1016/j.scitotenv.2017.06.031>.
- Bolam, T., Barry, J., Law, R.J., James, D., Thomas, B., Bolam, S.G., 2014. A temporal and spatial assessment of TBT concentrations at dredged material disposal sites around the coast of England and Wales. *Mar. Pollut. Bull.* 79, 326–332. <https://doi.org/10.1016/j.marpolbul.2013.12.003>.
- Brooke, D., Footitt, A., Nwaogu, T.A., 2004. Environmental Risk Evaluation Report: Perfluorooctanesulphonate (PFOS). Environment Agency.
- Centineo, G., Gonzalez, E.B., Sanz-Medel, A., 2004. Multielemental speciation analysis of organometallic compounds of mercury, lead and tin in natural water samples by headspace-solid phase microextraction followed by gas chromatography-mass spectrometry. *J. Chromatogr. A* 1034, 191–197. <https://doi.org/10.1016/j.chroma.2004.01.051>.
- Chen, C., Chen, L., Xue, R., Huang, Q., Wu, L., Ye, S., Zhang, W., 2019. Spatiotemporal variation and source apportionment of organotin compounds in sediments in the Yangtze Estuary. *Environ. Sci. Eur.* 31. <https://doi.org/10.1186/s12302-019-0207-z>.
- Chou, C.C., Lee, M.R., 2005. Determination of organotin compounds in water by headspace solid phase microextraction with gas chromatography-mass spectrometry. *J. Chromatogr. A* 1064, 1–8. <https://doi.org/10.1016/j.chroma.2004.08.166>.
- Cole, R.F., Mills, G.A., Parker, R., Bolam, T., Birchenough, A., Kröger, S., Fones, G.R., 2015. Trends in the analysis and monitoring of organotins in the aquatic environment. *Trends Environ. Anal. Chem.* <https://doi.org/10.1016/j.teac.2015.05.001>.
- Concha-Graña, E., Muniategui Lorenzo, S., López-Mahía, P., Prada-Rodríguez, D., 2017. Sonication and dispersive solid-phase extraction with liquid chromatography-LTQ Orbitrap high resolution mass spectrometry determination for the fast and sensitive analysis of PFOA, PFOS and PFOS precursors in sediment samples. In: Maria Llompart Vizoso Juan Pablo Lamas Castro, T.D. (Ed.), 19th International Symposium on Advances in Extraction Technologies. Santiago de Compostela, p. 225.
- Concha-Graña, E., Fernández-Martínez, G., López-Mahía, P., Prada-Rodríguez, D., Muniategui-Lorenzo, S., 2018. Fast and sensitive determination of per- and polyfluoroalkyl substances in seawater. *J. Chromatogr. A* 1555. <https://doi.org/10.1016/j.chroma.2018.04.049>.
- Delle Site, A., 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem.* 30, 187–439.
- Devos, C., David, F., Sandra, P., 2012. A new validated analytical method for the determination of tributyltin in water samples at the quantification level set by the European Union. *J. Chromatogr. A* 1261, 151–157. <https://doi.org/10.1016/j.chroma.2012.07.072>.
- DHI, Pedersen, A.R., Rasmussen, D., Bjergstrøm, Morten, 2014. Environmental Impacts of Certain Phthalates and Alternatives to Phthalates. Danish Environmental Protection Agency.
- Diez, S., Bayona, J.M., 2009. Butyltin occurrence and risk assessment in the sediments of the Iberian Peninsula. *J. Environ. Manag.* 90, S25–S30. <https://doi.org/10.1016/j.jenvman.2008.07.021>.
- Diez, S., Abalos, M., Bayona, J.M., 2002. Organotin contamination in sediments from the Western Mediterranean enclosures following 10 years of TBT regulation. *Water Res.* 36, 905–918. [https://doi.org/10.1016/s0043-1354\(01\)00305-0](https://doi.org/10.1016/s0043-1354(01)00305-0).
- EC, X., 2009. Commission Directive 2009/90/EC of 31 July 2009 Laying Down, Pursuant to Directive 200/60/EC of the European Parliament and of the Council, Technical Specifications for Chemical Analysis and Monitoring of Water Status.
- ECHA, 2019. ECHA/NR/19/26 (Endocrine disrupting properties to be added for four phthalates in the authorisation list).
- Eklund, B., Watermann, B., 2018. Persistence of TBT and copper in excess on leisure boat hulls around the Baltic Sea. *Environ. Sci. Pollut. Res.* 25, 14595–14605. <https://doi.org/10.1007/s11356-018-1614-1>.
- European Commission, 2018. Commission regulation 2018/2005 of 17 December 2018 amending annex XVII to regulation (EC) no 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). *Off. J. Eur. Union* 61 (L 322/14-L 322/19).
- European-Chemicals-Agency, 2016. (ECHA) Plastic additives initiative-Mapping exercise. <https://echa.europa.eu/es/mapping-exercise-plastic-additives-initiative>.
- European-Commission, 2020. Chemicals Strategy for Sustainability Towards a Toxic-Free Environment, COM(2020) 667 final Report.
- Fernández-González, V., Moscoso-Pérez, C., Muniategui-Lorenzo, S., López-Mahía, P., Prada-Rodríguez, D., 2017a. Rapid, simple and automatized method for the analysis of phthalates in sea water. 19th International Symposium on Advances in Extraction Technologies (ExTech 2017) (Santiago de Compostela (Spain)).
- Fernández-González, V., Moscoso-Pérez, C., Muniategui-Lorenzo, S., López-Mahía, P., Prada-Rodríguez, D., 2017b. Reliable, rapid and simple method for the analysis of

- phthalates in sediments by ultrasonic solvent extraction followed by head space-solid phase microextraction gas chromatography mass spectrometry determination. *Talanta* 162, 648–653. <https://doi.org/10.1016/j.talanta.2016.10.068>.
- Furdek, M., Vahčić, M., Ščančar, J., Milačić, R., Kniewald, G., Mikac, N., 2012. Organotin compounds in seawater and *Mytilus galloprovincialis* mussels along the Croatian Adriatic Coast. *Mar. Pollut. Bull.* 64, 189–199. <https://doi.org/10.1016/j.marpolbul.2011.12.009>.
- German Rodríguez, J., Solaun, O., Larreta, J., Belzunce Segarra, M.J., Franco, J., García Alonso, J.L., Sariego, C., Valencia, V., Borja, A., 2010. Baseline of butyltin pollution in coastal sediments within the Basque Country (northern Spain), in 2007–2008. *Mar. Pollut. Bull.* 60, 139–145. <https://doi.org/10.1016/j.marpolbul.2009.11.003>.
- Gómez, C., Vicente, J., Echavarrí-Erasun, B., Porte, C., Lacorte, S., Gomez, C., Vicente, J., Echavarrí-Erasun, B., Porte, C., Lacorte, S., 2011. Occurrence of perfluorinated compounds in water, sediment and mussels from the Cantabrian Sea (North Spain). *Mar. Pollut. Bull.* 62, 948–955. <https://doi.org/10.1016/j.marpolbul.2011.02.049>.
- Hassanzadeh, N., Sari, A.E., Khodabandeh, S., Bahramifar, N., 2014. Occurrence and distribution of two phthalate esters in the sediments of the Anzali wetlands on the coast of the Caspian Sea (Iran). *Mar. Pollut. Bull.* 89, 128–135. <https://doi.org/10.1016/j.marpolbul.2014.10.017>.
- Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., Duflos, G., 2017. Occurrence and effects of plastic additives on marine environments and organisms: a review. *Chemosphere* 182, 781–793. <https://doi.org/10.1016/j.chemosphere.2017.05.096>.
- Higgins, C.P., Field, A.J., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* 39, 3946–3956.
- Hong, S., Khim, J.S., Park, J., Kim, M., Kim, W.-K., Jung, J., Hyun, S., Kim, J.-G., Lee, H., Choi, H.J., Codling, G., Giesy, J.P., 2013. In situ fate and partitioning of waterborne perfluoroalkyl acids (PFAAs) in the Youngsan and Nakdong River Estuaries of South Korea. *Sci. Total Environ.* 445–446, 136–145.
- INERIS, 2008. Implementations of Requirements on Priority Substances Within the Context of the Water Framework Directive.
- Kwadijk, C., Korytar, P., Koelmans, A., 2010. Distribution of perfluorinated compounds in aquatic systems in the Netherlands. *Environ. Sci. Technol.* 44, 3746–3751.
- León, V.M., Viñas, L., Concha-graña, E., Fernández-gonzález, V., Salgueiro-gonzález, N., Moscoso-pérez, C., Muniategui-lorenzo, S., Campillo, J.A., 2020. Identification of contaminants of emerging concern with potential environmental risk in Spanish continental shelf sediments. *Sci. Total Environ.* 742, 140505. <https://doi.org/10.1016/j.scitotenv.2020.140505>.
- Liang, D.W., Zhang, T., Fang, H.H.P., He, J., 2008. Phthalates biodegradation in the environment. *Appl. Microbiol. Biotechnol.* 80, 183–198.
- Liu, P., Tian, T., Barreto, J., Chou, J., 2013. Assessment and analysis of phthalate esters, in Lake Pontchartrain, by SPME combining with GC-MS. *Environ. Technol.* 34, 453–462. <https://doi.org/10.1080/09593330.2012.698653>.
- Liu, H., Cui, K., Zeng, F., Chen, L., Cheng, Y., Li, H., Li, S., Zhou, X., Zhu, F., Ouyang, G., Luan, T., Zeng, Z., 2014. Occurrence and distribution of phthalate esters in riverine sediments from the Pearl River Delta region, South China. *Mar. Pollut. Bull.* 83, 358–365. <https://doi.org/10.1016/j.marpolbul.2014.03.038>.
- Lorenzo, M., Campo, J., Morales Suarez-Varela, M., Pico, Y., Suárez-Varela, M.M., Picó, Y., 2019. Occurrence, distribution and behavior of emerging persistent organic pollutants (POPs) in a Mediterranean wetland protected area. *Sci. Total Environ.* 646, 1009–1020. <https://doi.org/10.1016/j.scitotenv.2018.07.304>.
- Lv, J., Guo, C., Liang, S., Zhang, Y., Xu, J., 2019. Partitioning behavior, source identification, and risk assessment of perfluorinated compounds in an industry-influenced river. *Environ. Sci. Eur.* 31, 55.
- Malem, F., Soonthondech, P., Khawmodjod, P., Chunhakorn, V., Whitlow, H.J., Chienthavorn, O., 2019. Occurrence of phthalate esters in the eastern coast of Thailand. *Environ. Monit. Assess.* 191, 4–6. <https://doi.org/10.1007/s10661-019-7785-5>.
- Mejía Avedaño, S., Liu, J., 2015. Production of PFOS from anaerobic soil biotransformation of two perfluoroalkyl sulfonamide derivatives. *Chemosphere* 119, 1084–1090.
- Mhadhbi, L., Rial, D., Pérez, S., Beiras, R., 2012. Ecological risk assessment of perfluoroctanoic acid (PFOA) and perfluoroctanesulfonic acid (PFOS) in marine environment using *Isochrysis galbana*, *Paracetroutus lividus*, *Siriella armata* and *Psetta maxima*. *J. Environ. Monit.* 14, 1375–1382.
- Moscoso-Pérez, C., Fernández-González, V., Moreda-Piñeiro, J., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2015. Determination of organotin compounds in waters by headspace solid phase microextraction gas chromatography triple quadrupole tandem mass spectrometry under the European water framework directive. *J. Chromatogr. A* 1385, 85–93. <https://doi.org/10.1016/j.chroma.2015.01.070>.
- MSFD, 2008. Marine Strategy Framework Directive 2008/56/EC.
- Muniategui-Lorenzo, S., Moscoso-Pérez, C., Fernández-González, V., Moreda-Piñeiro, J., López-Mahía, P., 2019. Optimization of a MSPD-UAE-GC-QqQ-MS/MS method for the determination of organic tin compounds in sediments. XXV Encontro Galego-Portugues de Química (Santiago de Compostela (Spain)).
- OSPAR, 2006. Phthalates OSPAR Commission 2005 (2006 Update).
- OSPAR-Commission, 2011. Background Document on Organic tin compounds Hazardous Substances Series. Hazardous Substances Series.
- Palma, P., Koec-Schulmeyer, M., Alvarenga, P., Ledo, L., Barbosa, I.R., Lopez de Alda, M., Barcelo, D., Kock-Schulmeyer, M., Alvarenga, P., Ledo, L., Barbosa, I.R., Lopez de Alda, M., Barcelo, D., 2014. Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal). *Sci. Total Environ.* 488–489, 208–219. <https://doi.org/10.1016/j.scitotenv.2014.04.088>.
- Paluselli, A., Aminot, Y., Galgani, F., Net, S., Sempere, R., 2018a. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. *Prog. Oceanogr.* 163, 221–231. <https://doi.org/10.1016/j.pcean.2017.06.002>.
- Paluselli, A., Fauvel, V., Schmidt, N., Galgani, F., Net, S., Sempere, R., 2018b. Distribution of phthalates in Marseille Bay (NW Mediterranean Sea). *Sci. Total Environ.* 621, 578–587. <https://doi.org/10.1016/j.scitotenv.2017.11.306>.
- Perez-Ruzafa, A., Marcos, C., Gilabert, J., 2005. The ecology of the Mar Menor coastal lagoon: a fast changing ecosystem under human pressure. In: Gonenc, I.E., Wolfli, J.P. (Eds.), *Coastal Lagoons: Ecosystem Processes and Modeling for Sustainable Use and Development*. CRC Press.
- Perra, G., Focardi, S.E., Guerranti, C., 2013. Levels and spatial distribution of perfluorinated compounds (PFCs) in superficial sediments from the marine reserves of the Tuscan Archipelago National Park (Italy). *Mar. Pollut. Bull.* 76, 379–382. <https://doi.org/10.1016/j.marpolbul.2013.07.051>.
- Qi, Y., Huo, S., Xi, B., Hu, S., Zhang, J., He, Z., 2016. Spatial distribution and source apportionment of PFASs in surface sediments from five lake regions, China. *Sci. Rep.* 6. <https://doi.org/10.1038/srep22674>.
- Quinete, N., Wu, Q., Zhang, T., Yun, S.H., Moreira, I., Kannan, K., 2009. Specific profiles of perfluorinated compounds in surface and drinking waters and accumulation in mussels, fish, and dolphins from southeastern Brazil. *Chemosphere* 77, 863–869.
- Sanchez-Avila, J., Tauler, R., Lacorte, S., 2012. Organic micropollutants in coastal waters from NW Mediterranean Sea: sources distribution and potential risk. *Environ. Int.* 46, 50–62. <https://doi.org/10.1016/j.envint.2012.04.013>.
- Sanchez-Avila, J., Vicente, J., Echavarrí-Erasun, B., Porte, C., Tauler, R., Lacorte, S., 2013. Sources, fluxes and risk of organic micropollutants to the Cantabrian Sea (Spain). *Mar. Pollut. Bull.* 72, 119–132.
- Segovia-Martínez, L., Bouzas-Blanco, A., Campíns-Falcó, P., Seco-Torrecillas, A., 2010. Improving detection limits for organotin compounds in several matrix water samples by derivatization-headspace-solid-phase microextraction and GC-MS. *Talanta* 80, 1888–1893. <https://doi.org/10.1016/j.talanta.2009.10.039>.
- Taniyasu, S., Kannan, K., Wu, Q., Kwok, K.Y., Yeung, L.W.Y., Lam, P.K.S., Chittim, B., Kida, T., Takasuga, T., Tsuchiya, Y., Yamashita, N., 2013. Inter-laboratory trials for analysis of perfluorooctanesulfonate and perfluorooctanoate in water samples: performance and recommendations. *Anal. Chim. Acta* 770, 111–120.
- The-Conference-of-the-Parties, 2010. UNEP-POPS-COP-4-SC-4-17: Listing of Perfluorooctane Sulfonic Acid, Its Salts and Perfluorooctane Sulfonyl Fluoride.
- Thomaidis, N.S., Stasinakis, A.S., Gatidou, G., Morabito, R., Massaniso, P., Lekkas, T.D., 2007. Occurrence of organotin compounds in the aquatic environment of Greece. *Water Air Soil Pollut.* 181, 201–210. <https://doi.org/10.1007/s11270-006-9293-9>.
- Wang, T., Wang, Y.W., Liao, C.Y., Cai, Y.Q., Jiang, G.B., 2009. Perspectives on the inclusion of perfluoroctane sulfonate into the Stockholm convention on persistent organic pollutants. *Environ. Sci. Technol.* 43, 5171–5175.
- Wang, H.S., Du, J., Leung, H.M., Leung, A.O.W., Liang, P., Giesy, J.P., Wong, C.K.C., Wong, M.H., 2011a. Distribution and source apportionments of polychlorinated biphenyls (PCBs) in mariculture sediments from the Pearl River Delta, South China. *Mar. Pollut. Bull.* 63, 516–522.
- Wang, T., Lu, Y., Chen, C., Naile, J.E., Khim, J.S., Park, J., Luo, W., Jiao, W., Hu, W., Giesy, J.P., 2011b. Perfluorinated compounds in estuarine and coastal areas of north Bohai Sea, China. *Mar. Pollut. Bull.* 62, 1905–1914.
- Wang, Y., Li, F., Ruan, X., Song, J., Lv, L., Chai, L., Yang, Z., 2017. Biodegradation of di-n-butyl phthalate by bacterial consortium LV-1 enriched from river sludge. *PLoS One* 12.
- WFD, 2013. Water Framework Directive 2013/39/EU.
- White, N.D., Balthis, L., Kannan, K., De Silva, A.O., Wu, Q., French, K.M., Daugomah, J., Spencer, C., Fair, P.A., 2015. Elevated levels of perfluoroalkyl substances in estuarine sediments of Charleston, SC. *Sci. Total Environ.* 521, 79–89. <https://doi.org/10.1016/j.scitotenv.2015.03.078>.
- WHO, 2006. The World Health Organisation, Mono- and disubstituted methyltin, butyltin, and octyltin compounds. Concise International Chemical Assessment Document. 73.
- Wille, K., Vanden Bussche, J., Noppe, H., DeWulf, E., VanCaeter, P., Janssen, C.R., DeBrabander, H.F., Vanhaecke, L., 2010. A validated analytical method for the determination of perfluorinated compounds in surface-, sea- and wastewater using liquid chromatography coupled to time-of-flight mass spectrometry. *J. Chromatogr. A* 1217, 6616–6622.
- Xie, Z., Zhao, Z., Moeller, A., Wolschke, H., Ahrens, L., Sturm, R., Ebinghaus, R., 2013. Neutral poly- and perfluoroalkyl substances in air and seawater of the North Sea. *Environ. Sci. Pollut. Res.* 20, 7988–8000. <https://doi.org/10.1007/s11356-013-1757-z>.
- Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Okazawa, T., Petrick, G., Gamo, T., 2004. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. *Environ. Sci. Technol.* 38, 5522–5528.
- Zhang, K.G., Shi, J.B., He, B., Xu, W.H., Li, X.D., Jiang, G.B., 2013. Organotin compounds in surface sediments from selected fishing ports along the Chinese coast. *Chinese Sci. Bull.* 58, 231–237. <https://doi.org/10.1007/s11434-012-5406-6>.
- Zhang, Z.M., Zhang, H.H., Zou, Y.W., Yang, G.P., 2018. Distribution and ecotoxicological state of phthalate esters in the sea-surface microlayer, seawater and sediment of the Bohai Sea and the Yellow Sea. *Environ. Pollut.* 240, 235–247. <https://doi.org/10.1016/j.envpol.2018.04.056>.