



Coastal gradients of small microplastics and associated pollutants influenced by estuarine sources

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ARTICLE INFO

Keywords:

Marine litter
Microplastics
Estuarine sources
Oceanographic current
Metallic additives
Food web

ABSTRACT

Small microplastics (SMPs) in the gulf of Cadiz was sampled at 5 m depth by pumping it through the ship's pipe system and filtered through a 45 μm mesh size net. Our study reveals that higher densities have been found (130 $\text{mg}\cdot\text{m}^{-3}$) compared to other regions worldwide and these densities decreased from the coastline to the outer stations, showing a general coastal gradient influenced by estuarine outflows. SMPs with a size range between 45 and 193 μm were predominant and most of them composed by polyethylene and polypropylene. The metals associated with the MPs were mainly Na (21.1%), K (11.3%), Fe (8.5%), Ca (2.1%), Cr (1.8%), Zr (13.3%) and Hf (0.7%). The high proportion of Zr compared to Fe, which is different from what can be found in the environment, suggests that this metal is intrinsic to the materials used in catalytic processes during plastic production.

1. Introduction

Production of plastic in the world is overwhelming, reaching up to 368 million tonnes in 2019 (PlasticsEurope, 2020). Due to continuous leakage to the environment, plastic waste originates from diverse land sources (Hardesty et al., 2017; Lebreton et al., 2017), and persist in different marine ecosystems (Barnes et al., 2009). This contaminant represents a 95% of the total marine litter; (Galgani et al., 2015). However, and despite its magnitude, studies concerning plastics in the waters of many ocean regions, such as the southernmost European Atlantic regional sea in the Gulf of Cadiz (GoC), have not been published.

The plastic items most frequently found in the ocean are: food wrappings, containers, plastic bags, straws, stirrers, caps and lids, beverage bottles, cups, plates and cigarette filters (Bergmann et al., 2015). High-density polyethylene (HDPE), low-density polyethylene (LDPE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET) are the most common polymers of these plastic items produced on the market and consumed, and also the

polymers most commonly found in aquatic environments (Andrady, 2011; Engler, 2012). These plastics are known as “hard-to-degrade” materials and are able to persist in the natural environment for years and even centuries (Cole et al., 2011). However, primary plastics and their debris become fragmented and degraded when they are exposed to environmental agents such as UV light, waves and wind through photodegradation, oxidation or mechanical abrasion (Lambert and Wagner, 2016). The continuous fragmentation of plastic particles ends up with increasingly smaller sizes, microplastics (MPs) have been reported in all ocean areas from urban and industrialized coastal areas to remote zones (Ivar do Sul and Costa, 2014). Previous studies have showed evidence of very small MPs (<100 μm) in the water column (Cole et al., 2013; Ter Halle et al., 2017). These sizes are beyond the reach of the sampling methods generally used to collect MPs in the water column where most of the techniques used rely on neuston nets or manta nets (333 μm) to collect floating plastic debris (Cózar et al., 2014). The potential fragmentation of MPs into smaller pieces, sinking in the ocean, could explain their limited concentration and lack of increasing trends in the surface waters compared to modelled estimates (Cózar et al., 2014; Galgani

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<https://doi.org/10.1016/j.marpolbul.2021.113292>

Received 7 June 2021; Received in revised form 25 November 2021; Accepted 20 December 2021

Available online 7 January 2022

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et al., 2021).

Buoyant MPs are able to sink as part of faecal pellets and marine snow when ingested by marine organisms (Cole et al., 2016; Kooi and Koelmans, 2019). The quantity of small microplastics, (SMPs; range from 20 μm to 1 mm; Galgani et al., 2013; Erni-Cassola et al., 2017) is unknown or very little estimated (Ter Halle et al., 2017), especially those plastics in the surface waters that do not float and can be mostly found below the first meter of water. To investigate whether surface waters and the subsequent subsurface waters could be storing an important fraction of the lower size limit of MPs, a good representativeness of these MPs in the first meters of waters should be sampled and thus large volumes of seawater need to be processed (Montoto-Martínez et al., 2020). When Bongo's plankton nets are used at low velocities with a small mesh size ($\sim 100 \mu\text{m}$), they can quickly become clogged, although this allows the sampling of the water column if the net is hauled vertically. Sampling with neuston nets or manta nets (333 μm) only allows the sampling of surface water or the first meter of the water column, respectively (Prata et al., 2019). However, there is some evidence that subsurface oceanic waters may contain high microplastic abundances (Pabortsava and Lampitt, 2020) and sampling surface waters is insufficient to understand the distribution and fate of these particles (Miller et al., 2017; Montoto-Martínez et al., 2020). An alternative to nets includes water pumps that can be comprised by a vessel's intakes, deck pumps or even those used in coastal areas (Montoto-Martínez et al., 2020). Additionally, this method allows the choice of smaller mesh sizes (Prata et al., 2019). The distribution of plastic polymer types has revealed that low-density polymer types such as PE and PP are more abundant in open sea surface waters, but these polymers (PE and PP) were less abundant in intertidal- or subtidal samples (Erni-Cassola et al., 2019). Regarding the water column, plastics denser than seawater, such as polyester, polyamide (PA) and acrylics, were relatively more abundant in subsurface water than in sea surface waters (Erni-Cassola et al., 2019). Overall, two major groups were found recently for the subsurface ocean waters (4 m depth) of the Canary Island, fibers (64.42%) were predominant over fragments (35.58%), with the concentration values falling within the ranges of data reported for other areas of the Atlantic (Montoto-Martínez et al., 2020). Plastic debris adsorbs onto its surface persistent bioaccumulated toxic substances and inorganic metals from the surrounding environment, but furthermore they have incorporated intrinsically dozens of organic and inorganic additives during its fabrication to improve the physical properties of the polymer (Murphy, 2001; Sendra et al., 2021a). Therefore, from the extrinsic and intrinsic organic and inorganic substances present in plastic polymers, they can be recognized as a "soup of pollutants" (Sendra et al., 2021a). Among the most common additives, they are organized into groups of substances according to their industrial applications, for example, stabilizers, antioxidants and UV stabilizers, plasticisers, curing agents, brominated flame retardants, biocides, blowing agents, fillers, inorganic pigments, organic pigments, heat stabilizers, soluble colorants, reinforcements and slip agents (Sendra et al., 2021a).

The study of these additives is relevant, however marine environment have a chemical footprint. This footprint is conditioned by the organic and inorganic pollutants and xenobiotics in the surrounding environments. Pollutants can be adsorbed by SMPs due to polymers characteristics, therefore SMPs could be functioning as a vector of these substances in aquatic ecosystems, especially in those waters where the concentration of SMPs is high.

The prevalence and concentration of different plastic polymers in aquatic environments may be influenced by: geographic location such as local sources of pollution near marine environments, coastal regions with a high population density (Browne et al., 2010), distance to coast (Pedrotti et al., 2016), sampling depth (Eo et al., 2018), oceanographic characteristics, climatologic characteristics and periodic changes, for example: currents, waves, wind, pressure and tidal characteristics (Hardesty et al., 2017), the shape of the particles (Kooi et al., 2016) and, sampling methodology (Miller et al., 2017; Montoto-Martínez et al.,

2020). For instance, with regards to oceanographic conditions, a number of studies have shown that MPs tend to concentrate in the convergence zones of oceanic subtropical gyres (Cózar et al., 2014). At the moment, we do not know the concentration of SMPs in the GoC and how the complex oceanographic currents might influence the spatial distribution of those particles. This study is relevant considering that this area plays a key role in the exchanges of water between the North Atlantic Ocean and the Mediterranean Sea through the Strait of Gibraltar and thus in the final destiny of SMPs.

The objectives of this investigation were: i) to study the concentration, characterization and distribution of SMPs in subsurface waters at a depth of 5 m across the Gulf of Cadiz from the Guadiana estuary to the Cape of Trafalgar. ii) to analyze the metals (intrinsic or extrinsic source) on the surface of the SMPs, and iii) to establish relationships concerning the abundance of SMPs and environmental variables (geographic and physical factors).

2. Material and methods

2.1. Study area and sampling

Subsurface waters samples were collected in 13 transects distributed in radials from the GoC (southwest Spain), a semi-enclosed basin, whose oceanographic dynamics are mainly controlled by the exchanges between environmental sub-basins: the Mediterranean and Atlantic basins and the coastal system (Bellanco and Sánchez-Leal, 2016). Samples were taken in June 2019 from underwater transits while sailing the R/V Ramon Margalef during the scientific cruise STOCA 201906. (<http://datos.iew.es/geonetwork/srv/spa/catalog.search#/metadata/urn:SDN:CSR:LOCAL:29RM201906140>). The stations are the sampling points of the physical-chemical samples, and these sampling stations were distributed in radial transects with increasing distance from the coast (Fig. 1a). A ship's pump system was used to collect particulate material continuously from subsurface waters at a depth of 5 m from the research vessel while sailing (Supplementary Material), to an outlet equipped with a flow meter. This device consists of an on-board pump, reducer pipe, water flow meter, and metallic mesh as a sample collector. Water is pumped continuously from a fixed depth (5 m depth) to the sample collector on board the ship (Fig. 1). Its volume was measured and filtered through a 45 μm metallic mesh (Fig. 1b). Along each radial transect, an average of 7720 L of subsurface water were filtered per sample from a depth of 5 m, and the samples were stored at $-20 \text{ }^\circ\text{C}$.

2.2. Separation of microplastics

The samples (filtered through a 45 μm mesh size) were defrosted at room temperature ($25 \text{ }^\circ\text{C}$) in the laboratory, and samples followed the methodology described in Edo et al. (2020). Briefly explained; the filtered content was removed from the steel net using a steel spatula and ultrapure water and transferred to a 250 mL glass beaker. Due to the high amount of organic matter, a digestion was performed with a 10% (w/v) potassium hydroxide solution (KOH). KOH was added at a 1:3 volume to the sample. Then, the mixture was placed in an oven at $40 \text{ }^\circ\text{C}$ for 24 h. Since not all the organic matter was digested, a 15% solution of hydrogen peroxide was added at a 1:1 volume of the sample and the mixture was placed in an oven at $40 \text{ }^\circ\text{C}$ for 72 h. In some cases, it was necessary to leave the samples in the oven for a longer period of time. The organic matter was fully digested when the samples became transparent.

The samples were sieved using a 5 mm sieve to remove large particles. The range of plastic litter analyzed in this study was between 45 and 5000 μm . A NaCl solution (6.8 M) was added to increase the density of the aqueous solution and, as a result, the SMPs could be found floating in the suspension. After stirring the sample, the upper part of the aqueous solution was poured and filtered through 15 μm cellulose microfibre filters (Albet 140) with a vacuum pump. In addition, the walls of

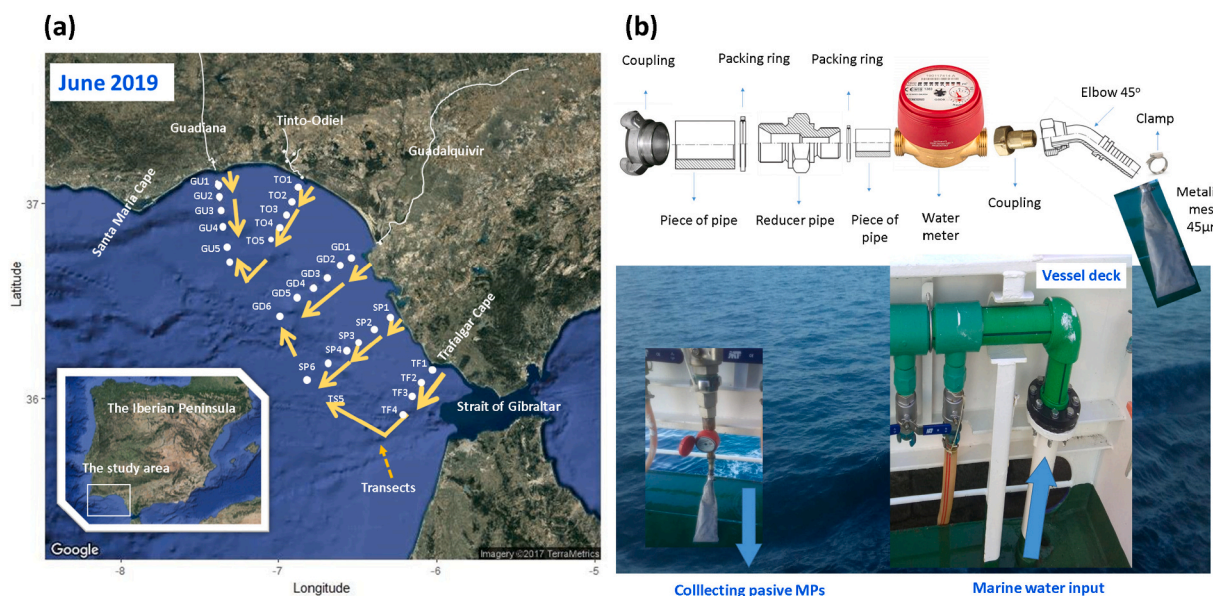


Fig. 1. (a) Maps of the Gulf of Cadiz showing the location of sampling sites and radials from right to left: TF Trafalgar, SP Sancti Petri, GD Guadalquivir, TO Tinto-Odiel, and GU Guadiana. The points indicate the sample locations of physical factors and the arrows the radial transects for microplastic sampling. (b) The device with details of the parts used to collect MPs from 5 to 10 m depth on a moving ship.

the glass were washed with ultrapure water (MQ water) and the cleaning solution was also filtered. All the microplastics were placed on the filters and were then dried at 40 °C for 48 h and stored in Petri dishes. The filters were weighed before and after the samples were collected (dried) to estimate the mass of plastic particles and determine the concentration (mg m^{-3}) of SMPs. Microplastics below 45 μm were found after digestion.

Process blanks were used to determine if any contamination was present during the processing of the samples. This consisted of running all the steps with the same procedure. The process blank only contained 0.004 ± 0.008 g. This mass was subtracted from the total weight of all filter. In this way we can know the mass only due to plastic items. In addition, a positive control with 0.1 g of polystyrene particles ($\sim 100 \mu\text{m}$ size) was used to test the recovery rate of the method, and a $99.267 \pm 0.386\%$ was recorded.

2.3. Analytical methods: FTIR, SEM, optic microscopy and XRF analysis

The polymers in a range from 45 to 5000 μm located on the filters were studied. The filters were milled and homogenized to proceed with the analysis. Identification of the polymers was performed by Fourier-transform infrared spectroscopy (FTIR) using the software Bruker Alpha System. Signals were obtained in transmittance mode and the spectral range was set at 4000 to 500 cm^{-1} . The resulting spectra were compared with the databases provided by Bruker company with a similarity higher than 40%. The samples were collected on filters and measured. In each case, the spectrum of the clean filter was subtracted.

Measuring the MPs was performed using Scanning Electron Microscopy (SEM), an Optic Microscope. The microscopes used were a Nova NanoSEM 450 model with a low voltage in low vacuum mode and a Nikon model EPIPHOT 200. Particle size distributions were obtained with the measurement of more than 100 particles from each station's sample. The MPs were selected randomly and measured in order to know the size distribution per radial transect. The size of the plastic fragment was measured from the maximum size of them independently of the particle shape.

The metallic additives of the MPs were identified by X-ray fluorescence analysis (XRF) in a Bruker S4 Pioneer spectrometer. The measurements were carried out directly on the filter, which do not have an XRF signal as they are made of light elements. This technique can be

used to analyze elements with an atomic number higher than 8.

2.4. Data analysis

Spatial analysis of the concentrations of MPs was conducted with the software Ocean data view (ODV) using the Data-Interpolating Variational Analysis (DIVA) method (Schlitzer, 2002). The non-parametric multivariate techniques of the distance-based linear modeling package (DISTLM) contained in PRIMER 6.1 (Plymouth Routines in Multivariate Ecological Research) were used to explore the relationships between the concentrations of SMPs from all the sampling stations and the environmental variables at the same sampling depth (Table S11). These were water temperature ($^{\circ}\text{C}$), chlorophyll *a* fluorescence (mg m^{-3}), dissolved oxygen (mg L^{-1}) (d) salinity, the number of each station within the radial as a proxy of the distance to the coast (Station) and radial along a north-south latitudinal variation (Radial).

DISTLM produces a marginal test, which assesses the variation each predictor (environmental variable and additives) has on its own, and a sequential test, assessing the variation of all the environmental variables (McArdle and Anderson, 2001). The most parsimonious model was identified using the AIC selection criterion and stepwise selection was used to determine the relative importance of the predictors. Distance-based redundancy analyses (dBRDA) were used to visualize the results as an ordination, constrained to linear combinations of the environmental variables. The DISTLM was run with 9999 permutations. Linear regression models were used to evaluate differences in the total concentrations of: microplastics, each plastic type (univariate data) between stations and radials using the robust statistical test multcomp and the sandwich package in R, which makes post hoc comparisons between different stations and radials for unbalanced data (Herberich et al., 2010) possible.

3. Results

3.1. Concentration, size and type of SMPs

The mean concentration of the SMPs in the subsurface water (5 m depth) of the GoC was 30.5 mg m^{-3} with a range between 3.5 and 130.5 mg m^{-3} , and it showed a clear spatial pattern in relation to the distance from the coast (Fig. 2a, b). The concentration of SMPs differed

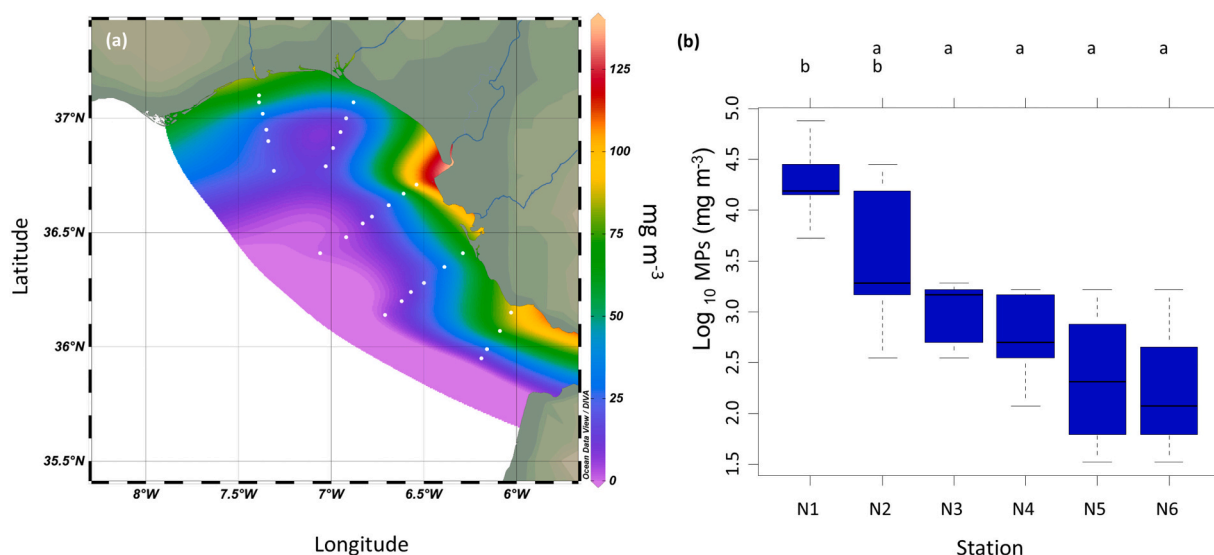


Fig. 2. (a) Map of in situ SMPs concentrations for the cruise as obtained using the Data-Interpolating Variational Analysis (DIVA) method. Color bars indicate mg m^{-3} . (b) Box plots describing the concentrations of SMPs (\log_{10} -transformed, mg m^{-3}) in relation to the distance from the coast. Values of SMPs (Table S11) from the radial transects were associated with physical factors of the sample locations. Number of each station within radial as a proxy of the distance to the coast (from station number 1 close to the coastline to station number 6, further offshore). Middle line = median; upper edge = 75th percentile; lower edge = 25th percentile; lines = variability outside the quartiles; circles = outliers.

significantly between stations across all radial groups ($R = 0.46$, $p \leq 0.01$) but not between radial groups across all station groups ($R = 0.25$, $p = 0.05$) (Figure S11). The DISTLM marginal analysis of the total concentration of SMPs indicated that not all environmental variables were significant (Table S12). The variable “Station”, as a proxy of the distance to the coast, contributed considerably to the variation observed. DISTLM sequential tests with a step-wise procedure were run for concentration of SMPs and environmental variables for the GoC. The optimal model included the factor “Station” explaining 40% of the overall variation (Table S12 and Figure S11).

The average particle size was $67 \mu\text{m}$, ranging from 45 to $193 \mu\text{m}$ (Fig. 3a). Overall, the spatial distribution of mean particle size showed higher values at the stations associated to the coastline, such as the mouths of the Gadiana and Guadalquivir estuaries (with the exception of the Tinto-Odiel estuary), and on the coastline of the Trafalgar radial. The mean particle size showed an increase, compared to the other

radials (Fig. 3a), at the offshore stations of the Guadalquivir radial. It is worth highlighting that the variability in the particle size was higher at the stations where the bigger particle sizes were found, mainly in the Guadalquivir radial (Fig. 3b). The SEM and Optical microscope images revealed the presence of irregular shaped particles like brittle fragments or films (Supplementary Figure S12). The proportion of filaments (e.g. fibers) was very low in relation to brittle fragments or films. The fragments had granulated or cracked surfaces (Supplementary Figure S12).

FTIR analysis of these SMPs showed quite homogeneous spectra among all the samples, indicating that the composition of the types of plastic was similar (Fig. 4a; Supplementary Figure S13). Absorption bands around 2900 and 1450 cm^{-1} correspond to the presence of PE, PP, poly (1-butene) and cyclohexane derivatives. However, above 1650 cm^{-1} , the spectra presented a medium intensity band that does not correspond to any of them but could be assigned to PET or polyester. The presence of these plastics seemed to be confirmed by the appearance of

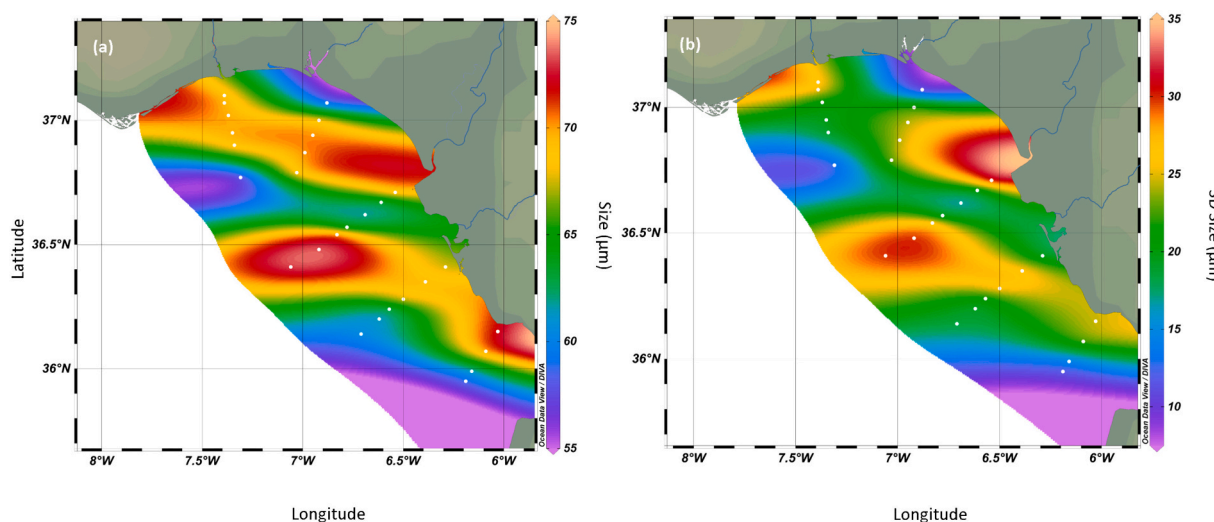


Fig. 3. (a) Spatial distribution of mean SMPs size for the cruise in the Gulf of Cadiz (GoC) obtained using the Data-Interpolating Variational Analysis (DIVA) method. Color bars indicate mean particle size in μm . (b) Spatial distributions of standard deviation (SD) value of SMPs size for the cruise in the GoC. Color bars indicate SD in μm .

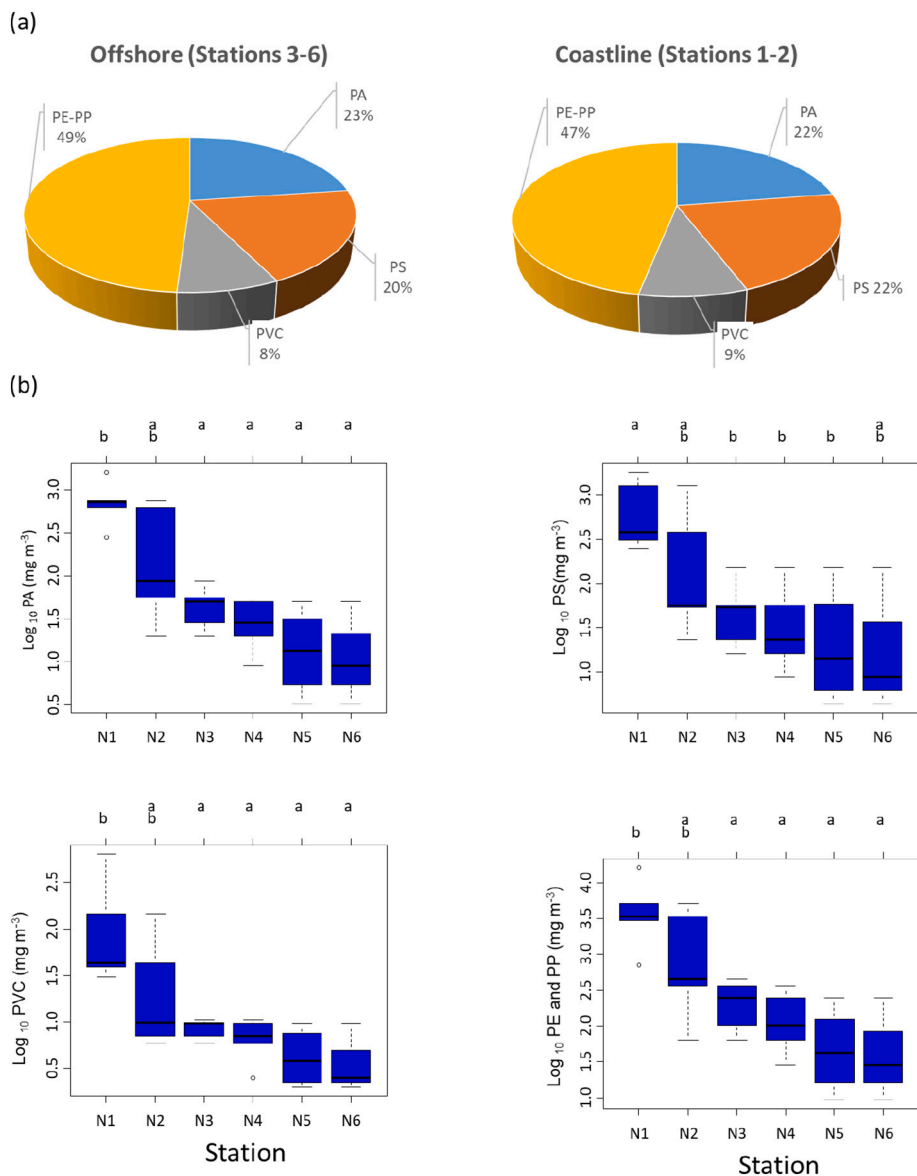


Fig. 4. (a) Percentage type of SMPs at offshore (station 3–6) and coastline (stations 1–2) stations found in the Gulf of Cadiz and (b) Box plots describing the plastic type concentrations (log₁₀-transformed, mg m⁻³) at each station sampled. Number of each station within radial as a proxy of the distance to the coast (from station number 1 close to the coastline to station number 6, further offshore). Middle line = median; upper edge = 75th percentile; lower edge = 25th percentile; lines = variability outside the quartiles; circles = outliers.

an intense band at 1050 cm⁻¹. Overall, the composition of the types of plastic was similar at each sampling station; the plastic polymers most frequently detected were PE and PP (40.4–52.5%). The other polymers found, in decreasing order, were PS (16.8–34.6%), PA (16.5–26.2%) and PVC (5.8–12.9%). The abundance of the five types of plastic followed a similar spatial pattern to the total concentration of SMPs (Fig. 4b). That is, the five types of plastics showed a gradual decrease in their concentrations between the stations close to the coast (1 and 2) and the offshore stations (3–7) and these differences were statistically significant, despite being smaller in the case of PS (Fig. 4b). A maximal dissimilarity was observed between the stations close to the coast (1 and 2) and the rest of the stations (60% dissimilarity), PP and PE were the polymers that contributed the most to this variability between stations (contribution range 43.3–50.5%).

3.2. Metals associated with the SMPs

The elements detected by XRF were Cl (39.6%), Na (21.1%), K (11.3%), Zr (13.3%), Fe (8.5%), Ca (2.1%), Cr (1.8%), Y (0.9%), Hf (0.7%), Zn (0.41%) and in a low proportion Al, Si, Ti, Ni, Mn, Sr, Br and Rh (0.1%) (Fig. 5). Those elements associated with the SMPs can be

divided in two main groups: (a) Na, Cl, K and Ca which may come from seawater residues or from the separation process; (b) and the rest of metals analyzed which could be intrinsic to the SMPs (mainly, Zr, Cr, and Fe) or due to the adsorption of anthropogenic trace metals from the seawater.

4. Discussion

4.1. SMPs in the waters of the Gulf of Cadiz shelf

MPs have been reported in all ocean areas from urban and industrialized coastal areas to remote zones (Ivar do Sul and Costa, 2014). Previous studies have showed evidence of very small MPs (<100 μm) in the water column (Cole et al., 2013; Ter Halle et al., 2017). Despite this fact, currently, not many studies have sampled SMPs with a mesh size below 100 μm in the water column, since most of them have largely focused on nets with >333 μm (Table SI3). The degradation pathways of plastic litter, the environmental fate at the small size scale of μm from their source to their final destination, and the subsurface distribution are important concerns to consider in SMPs studies (Ter Halle et al., 2017). Without a doubt, the continued fragmentation of the plastic particles

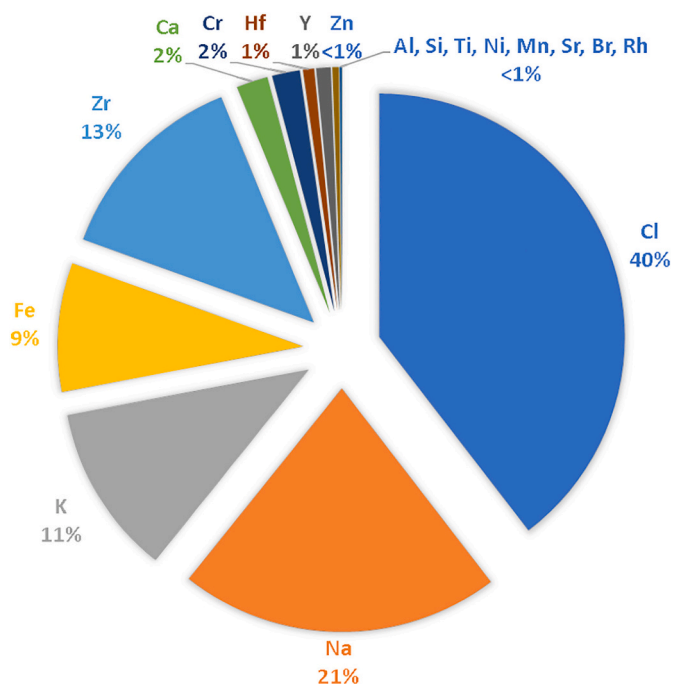


Fig. 5. Percentage distribution of metals in SMPs analyzed by XRF.

results in increasingly smaller sizes that are probably beyond the common sampling methods used to collect MPs in the water column (mesh size $>333 \mu\text{m}$). Therefore, developing a sampling system with a water pump to collect particulate material continuously from below the surface water and coupled to a counter to measure the filtered water could enable sampling SMPs $<1000 \mu\text{m}$ with a suitable mesh size (Prata et al., 2019). Our study is the first to investigate the occurrence and extent of the contamination by SMPs in subsurface waters at a depth of 5 m collected at both nearshore and offshore regions of the coastal area of the GoC. This approach could be used in other regions in order to obtain data concerning SMPs in seawater and their spatial distribution in relation to sources.

There is a diversity of methods used to collect MPs due to the difficulties of sampling MPs from the marine environment, in particular the limitations associated with sampling and characterization of the plastic particles at the microscale in natural samples (Table SI3). When we compare our data with that from other regions, we find that most of the studies quantified MPs by estimating the number of particles or their concentration in relation to the surface of water collected (Table SI3), hindering data comparison. One of the few studies analyzing SMPs at different depths, pumping large water volumes through a $55 \mu\text{m}$ stainless-steel mesh in open waters of the Atlantic Ocean, measured concentrations ranging $0.26\text{--}1.97 \text{ mg m}^{-3}$ at 10 m depth (Pabortsava and Lampitt, 2020), which are levels one to three orders of magnitude lower than those observed in the GoC.

Overall, it would be expected that sampling with a smaller mesh size could collect more MPs compared to a bigger mesh size (Lozano and Mouat, 2009). A recent study showed that reducing the sampling mesh size to $100 \mu\text{m}$ can increase microplastic concentration in numbers by 2.5-fold and 10-fold compared to $333 \mu\text{m}$ and $500 \mu\text{m}$ mesh size nets, respectively (Lindeque et al., 2020). The lack of harmonized monitoring and reporting of results for different particle size ranges and units prevent from direct comparisons for the assessment of the microplastics pollution levels found in the GoC. In any case, it has also been documented that SMPs are very abundant in the North Atlantic Subtropical gyre and that their concentration in weight is of the same order of magnitude as that of larger microplastics (Poulain et al., 2019). In shallow waters affected by anthropogenic activities, the presence of

SMPs at 5 m could be extended from the surface to deeper layers at a similar concentration range, due to their floatability properties, exposure to weathering and biofouling processes that facilitate sinking of small particles (Dai et al., 2018). Under these assumptions, there may be large quantities of SMPs suspended in the water column of coastal areas, so far underestimated or not accounted for, which are continuously available to organisms and could cause potential impacts on different trophic levels (Carbery et al., 2018; Walkinshaw et al., 2020). This is of particular interests in areas of high productivity and extraction of commercial species (e.g. small pelagics) such as the GoC (Baldó et al., 2006; Casaucao et al., 2021).

4.2. Sources, spatial distribution and fate of SMPs in waters of the Gulf of Cadiz shelf

The sources of SMPs in the GoC were associated mainly with human inputs from the Guadalquivir and Guadiana estuaries. Overall, plastics could be entering the marine environment mostly via rivers and estuaries (Ivar do Sul and Costa, 2014; Lebreton et al., 2017; González-Fernández et al., 2021). Coastal areas and especially estuarine systems affected by anthropogenic activities have been identified as MP hotspots (Wright et al., 2013; Sutton et al., 2016; Bikker et al., 2020; Hitchcock and Mitrovic, 2019; Wang et al., 2021). In the GoC, the highest concentrations of MPs occurred close to the Guadiana and Guadalquivir estuaries with concentrations of 64.6 and $130.5 \text{ mg}\cdot\text{m}^{-3}$, respectively, and in addition, these estuaries showed a great variety of size in the range studied. Specifically, in the case of the samples collected close to the Guadalquivir estuary, the highest concentration represented approximately 8 times the average concentration recorded along the continental shelf.

The transport of particles is a function of their size, shape and concentration, and these properties largely determine the minimum velocity of water that is required for their transport (Browne et al., 2011). Among the estuaries in the GoC, the Guadalquivir estuary basin has high sediment loads (González-Ortegón et al., 2019), and the highly turbid nature of this river compared with other rivers reaching the GoC could support a better transport, and thus higher values of SMPs in suspension. Therefore, although we do not know the relative importance of the different sources on the GoC, our data suggest that at least the surface waters of these estuaries, and potentially upstream the Guadalquivir River, represent an important pathway of SMPs to the GoC. Furthermore, the fact that this first evaluation of SMPs in the subsurface water of the GoC was made in early summer, when freshwater discharges decreased in these basins (Figure SI4), could indicate that these micro-pollutants might be retained in these tidal-dominated estuaries (Díez-Minguito et al., 2012; Caballero and Navarro, 2018). Thus, we could be underestimating the variability of SMPs concentrations in the GoC along the year, receiving much higher riverine inputs during the rainy season (Lebreton et al., 2017). We highlight that, given the presence of SMPs in all samples, with general decreasing concentrations from river mouths to offshore stations, estuarine waters are emitting large amounts of plastic particles that have already been subject to degradation and fragmentation processes in the river basins before reaching the marine environment. We hypothesize that, the general decrease in SMPs size with increasing distance from the coast is caused by vertical sorting mechanisms under different environmental conditions (floatability affected by salinity, wind and waves) and processes such as biofouling and interaction with lower trophic levels, where, at similar particle shapes and polymer densities, larger particles are physically faster and more stable to float or sink (Kooi et al., 2017; Kowalski et al., 2016).

Among the different types of MPs, PE and PP are more abundant on surface waters at open sea (Erni-Cassola et al., 2019) and are major components of the micro-pollutants transported to the coastal zone by rivers (e.g. Vianello et al., 2013). Previous studies of coastal waters have confirmed that these types of MPs are predominant (Cincinelli et al., 2017). In addition, plastics denser than seawater, such as PA, are

relatively more abundant in subsurface waters than on the surface (Erni-Cassola et al., 2019). This way, PA is a relatively important (22%) polymer in the subsurface water of the GoC at 5 m depth.

The decrease in the concentrations of SMPs from the coastline to the offshore waters of the continental shelf of the GoC is a common pattern and consistent with other studies (e.g. Pedrotti et al., 2016). The relatively high continental runoff near the large estuaries, in this case from the Cadiz Bay, and Guadiana and Guadalquivir estuaries, could provide high concentrations of SMPs along the inner shelf and thus, explain the spatial pattern of the SMPs. In oceans, the accumulation of plastic debris has been observed in the large-scale subtropical convergence zones due to the circulation of ocean currents (Law et al., 2010). The existence of a summer cyclonic period between the mouth of the Guadalquivir River and Cape Santa Maria (García-Lafuente et al., 2006) could help redistribute and retain MPs in the study area. This first assessment of MPs in the GoC is based on a fixed snapshot. It is relevant to understanding the dispersal patterns of SMPs and evaluate their potential impact on their distribution in future studies. Although tracing the distribution of MPs to their source is beyond the scope of the study, the present description allows us to highlight a number of interesting aspects of the surface circulation. The summer of 2019 was characterized by a persistent, cold eastward current along the mid shelf, resembling the Gulf of Cadiz Current (GCC) (Peliz et al., 2009), leaving a relatively tranquil region shoreward, likely affected by a westward, inshore countercurrent (Peliz et al., 2007). The GCC, which is shown in Figure S15, carries relatively cold, recently upwelled water east of Cape St. Vicente and C. St. Maria (Relvas and Barton, 2002) and extends further along the shelf-break into the Strait of Gibraltar (Peliz et al., 2007). This current may act both as a conveyor of MPs from the western shelf into the Mediterranean basin and as barrier between the inshore and oceanic domains.

Near Cape Trafalgar, a persistent, upwelling spot induced by tidal flow (Vargas-Yáñez et al., 2002) could explain the local increase in the concentration of relatively large size SMPs. Although, in nature, these processes of continental runoff and upwelling are typical of the fertilization of coastal waters, in this case, they may be accompanied by the resuspension of “artificial” items which, due to their small size, are easy prey for the marine biota (Lopes et al., 2020). Small fragments of plastic litter have been internalized by organisms at different levels in the food web such as primary producers and bacteria (Sendra et al., 2019; Gambardella et al., 2019), bivalves (Sendra et al., 2021b), crustaceans (Sendra et al., 2020a) and fish (Sendra et al., 2020b) triggering undesirable effects.

4.3. Inorganic metal additives in the SMPs of the GoC

Most of elements detected by XRF were relatively low mass seawater ions, for instance Na and Cl, although it is likely that residues remain from the separation process. However, metals were also found in the samples. The origin of metals could be due to the adsorption of trace metals to plastics suspended in the marine environment (Brennecke et al., 2016; Silva et al., 2018) or/and plastic additives incorporated over polymer production. Even though the particles present a low surface area and are inert, there are studies that indicate that they are capable of adsorbing large amounts of metals (Brennecke et al., 2016; Holmes et al., 2012). In addition, plastic polymers production can incorporate metal additives with different purposes: lead and cadmium as stabilizers, antioxidant, UV stabilizers and heat stabilizers; antimony, arsenic and cooper as biocides, zinc oxide as fillers; and aluminum, iron dioxide, titanium dioxide and Zinc oxide as inorganic pigments (Sendra et al., 2021a). All these metals are used to improve the physical and chemical properties of the polymer (Murphy, 2001).

The presence of metals in seawater may be very variable. From 1963 to 1995 the concentration of Fe, Cu, Ag, Au, Pb and Bi (in the range of nM) has decreased in the ocean until 180 times in 32 years (Ansari et al., 2004). For instance, the metals are characterized to have specific gravities from 4.5 (Ti) to 22.5 (Os). Therefore, the most of them tend to

the sedimentation in the soil (Ansari et al., 2004). A few recent studies have characterized dissolved trace metal concentrations in the GoC and in the three main rivers (González-Ortegón et al., 2019; Laiz et al., 2020). Although it could be expected an extrinsic origin of some elements, probably metals with high concentrations in the GoC (e.g. Fe and Cd), is important to consider that the years of sampling between those studies in the GoC and the current study were different, and thus the proportions of metals may vary. In fact, the composition of the dissolved trace metals in the GoC was very different from the metals obtained from the SMPs in this study. Several metallic elements associated to the catalytic process of the polymer production itself appeared in the current study. For example, Fe and Cr are characterized by good heat stability, excellent chemical resistance and bright colors (Murphy, 2001). Other elements analyzed in the SMPs could have a similar origin, i.e. Zr and Hf, which are known to be part of the Kaminsky catalyst (Kaminsky, 2013). A Kaminsky catalyst is a catalytic system for alkene polymerization to produce the polymer, and traces of Zr are found in the catalyst residues of commercial polyethylene (Bichinho et al., 2005). The fact that these elements, mainly Zr compared to Fe, appeared in higher proportions on the plastic particles than in the seawater suggests an intrinsic origin.

Funding

Financial support to EGO and the instrument was given by CSIC through Intramural Research program 2018 under grant number 201830I081. MS is grateful to the Spanish Ministry of Science, Innovation and Universities for the Juan de la Cierva (TJFI-2017-32493) contract. DGF was funded by European Union’s H2020-MSCA-IF-2018 846843—LitRivus.

CRedit authorship contribution statement

EGO set the conceptual framework of this study. EGO, FB and RS carried out the samplings. MS and MPY established the design of the analysis in the lab. ES, IR and MPY analyzed samples in the Lab. EGO analyzed the data. EGO and MS wrote the manuscript. EGO, MS, ES, RS, DGF and MPY reviewed the manuscript. All authors contributed to the final version of the manuscript.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Acknowledgments

The authors would like to thank the crew of the research vessels (B/O) Ángeles Alvariño, STOCA project and the STOCA 201906 Survey (IEO) and Jon Nesbit for proofreading the English text.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2021.113292>.

References

- Andrady, A.L., 2011. Microplastics in the marine environment. *Mar. Pollut. Bull.* 62 (8), 1596–1605.
- Ansari, T.M., Marr, I.L., Tariq, N., 2004. Heavy metals in marine pollution perspective—a mini review. *J. Appl. Sci.* 4 (1), 1–20.
- Baldó, F., García-Isarch, E., Jiménez, M.P., Romero, Z., Sánchez-Lamadrid, A., Catalán, I. A., 2006. Spatial and temporal distribution of the early life stages of three commercial fish species in the northeastern shelf of the Gulf of Cádiz. *Deep-Sea Res. II Top. Stud. Oceanogr.* 53, 1391–1401. <https://doi.org/10.1016/j.dsr2.2006.04.004>.

- Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. *Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci.* 364 (1526), 1985–1998.
- Bellanco, M.J., Sánchez-Leal, R.F., 2016. Spatial distribution and intra-annual variability of water masses on the eastern gulf of Cadiz seabed. *Cont. Shelf Res.* 128, 26–35.
- Bergmann, M., Gutow, L., Klages, M., 2015. In: *Marine Anthropogenic Litter*. Springer-Verlag, Berlin, p. 447.
- Bichinho, K.M., Pires, G.P., Stedile, F.C., dos Santos, J.H.Z., Wolf, C.R., 2005. Determination of catalyst metal residues in polymers by X-ray fluorescence. *Spectrochim. Acta B* 60 (5), 599–604.
- Bikker, J., Lawson, J., Wilson, S., Rochman, C.M., 2020. Microplastics and other anthropogenic particles in the surface waters of the Chesapeake Bay. *Mar. Pollut. Bull.* 156, 111257 <https://doi.org/10.1016/j.marpolbul.2020.111257>.
- Brennecke, D., Duarte, B., Paiva, F., Cacador, I., Canning-Clode, J., 2016. Microplastics as vector for heavy metal contamination from the marine environment. *Estuar. Coast. Shelf Sci.* 178, 189–195.
- Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T., et al., 2011. Accumulation of microplastic on shorelines worldwide: sources and sinks. *Environ. Sci. Technol.* 45 (21), 9175–42.
- Caballero, I., Navarro, G., 2018. Application of extended full resolution MERIS imagery to assist coastal management of the area adjacent to the Guadalquivir estuary. *Prog. Oceanogr.* 165, 215–232.
- Carbery, M., O'Connor, W., Palanisami, T., 2018. Trophic transfer of microplastics and mixed contaminants in the marine food web and implications for human health. *Environ. Int.* <https://doi.org/10.1016/j.envint.2018.03.007>.
- Casaucó, A., González-Ortegón, E., Jiménez, M.P., Teles-Machado, A., Plecha, S., Peliz, A.J., Laiz, I., 2021. Assessment of the spawning habitat, spatial distribution, and lagrangian dispersion of the european anchovy (*Engraulis encrasicolus*) early stages in the Gulf of Cadiz during an apparent anomalous episode in 2016. *Sci. Total Environ.* 781, 146530.
- Cincinelli, A., Scopetani, C., Chelazzi, D., Lombardini, E., Martellini, T., Katsoyiannis, A., et al., 2017. Microplastic in the surface waters of the Ross Sea (Antarctica): occurrence, distribution and characterization by FTIR. *Chemosphere* 175 (391–400), 9179.
- Cole, M., Lindeque, P., Halsband, C., Galloway, T.S., 2011. Microplastics as contaminants in the marine environment: a review. *Mar. Pollut. Bull.* 62 (12), 2588–2597.
- Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., et al., 2013. Microplastic ingestion by zooplankton. *Environ. Sci. Technol.* 47 (12), 6646–6655.
- Cole, M., Lindeque, P.K., Fileman, E., Clark, J., Lewis, C., Halsband, C., et al., 2016. Microplastics alter the properties and sinking rates of zooplankton faecal pellets. *Environ. Sci. Technol.* 50 (6), 3239–3246.
- Cózar, A., Echevarría, F., González-Gordillo, J.I., Irigoien, X., Úbeda, B., Hernández-León, S., et al., 2014. Plastic debris in the open ocean. *Proc. Natl. Acad. Sci. U. S. A.* 111 (28), 10239–10244.
- Dai, Z., Zhang, H., Zhou, Q., Tian, Y., Chen, T., Tu, C., Fu, C., Luo, Y., 2018. Occurrence of microplastics in the water column and sediment in an inland sea affected by intensive anthropogenic activities. *Environ. Pollut.* 242, 1557–1565.
- Díez-Minguito, M., Baquerizo, A., Ortega-Sánchez, M., Navarro, G., Losada, M.A., 2012. Tide transformation in the Guadalquivir estuary (SW Spain) and process-based zonation. *J. Geophys. Res. Oceans Atmos.* 117 (3), C03019.
- Edu, C., González-Pleiter, M., Leganés, F., Fernández-Piñas, F., Rosal, R., 2020. Fate of microplastics in wastewater treatment plants and their environmental dispersion with effluent and sludge. *Environ. Pollut.* 259, 113837.
- Engler, R.E., 2012. The complex interaction between marine debris and toxic chemicals in the ocean. *Environ. Sci. Technol.* 46 (22), 12302–12315.
- EO, S., Hong, S.H., Song, Y.K., Lee, J., Shim, W.J., 2018. Abundance, composition, and distribution of microplastics larger than 20 µm in sand beaches of South Korea. *Environ. Pollut.* 238, 894–902.
- Erni-Cassola, G., Gibson, M.I., Thompson, R.C., Christie-Oleza, J.A., 2017. Lost, but found with Nile red: a novel method for detecting and quantifying small microplastics (1 mm to 20 µm) in environmental samples. *Environ. Sci. Technol.* 51, 13641–13648. <https://doi.org/10.1021/acs.est.7b04512>.
- Erni-Cassola, G., Zadjelovic, V., Gibson, M.I., Christie-Oleza, J.A., 2019. Distribution of plastic polymer types in the marine environment: a meta-analysis. *J. Hazard. Mater.* 369, 691–698.
- Galgani, F., Hanke, G., Werner, S., Oosterbaan, L., Nilsson, P., Fleet, D., Kinsey, S., RC, T., Van Franeker, J., Vlachogianni, T., Scoullou, M., Mira Veiga, J., Palatinus, A., Matiddi, M., Maes, T., Korpinen, S., Budziak, A., Leslie, H., Gago, J., Liebezeit, G., 2013. Guidance on monitoring of marine litter in European seas, JRC scientific and policy reports, report EUR 26113 EN. In: *Guidance on Monitoring of Marine Litter in European Seas*. <https://doi.org/10.2788/99475>.
- Galgani, F., Hanke, G., Maes, T., 2015. Global distribution, composition and abundance of marine litter. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), *Marine Anthropogenic Litter*. Springer International Publishing, Cham, pp. 29–56. https://doi.org/10.1007/978-3-319-16510-3_2.
- Galgani, F., Brien, A.S.O., Weis, J., Ioakeimidis, C., Schuyler, Q., Makarenko, I., Bebianno, M.J., 2021. Are litter, plastic and microplastic quantities increasing in the ocean? *Microplastics Nanoplastics* 1 (1), 1–4.
- Gambardella, C., Piazza, V., Albertosa, M., Bebianno, M.J., Cardoso, C., Faimali, M., Sendra, M., 2019. Microplastics do not affect standard ecotoxicological endpoints in marine unicellular organisms. *Mar. Pollut. Bull.* 143, 140–143.
- García-Lafuente, J., Delgado, J., Criado-Aldeanueva, F., Bruno, M., del Río, J., Miguel Vargas, J., 2006. Water mass circulation on the continental shelf of the Gulf of Cádiz. *Deep-Sea Res. II Top. Stud. Oceanogr.* 53, 1182–1197.
- González-Fernández, D., Cózar, A., Hanke, G., Viejo, J., Morales-Caselles, C., Bakiri, R., Barceló, D., Bessa, F., Bruge, A., Cabrera, M., Castro-Jiménez, J., Constant, M., Crosti, R., Galletti, Y., Kideys, A.E., Machitadze, N., Pereira de Brito, J., Pogojeva, M., Ratola, N., Rigueira, J., Rojo-Nieto, E., Savenko, O., Schöneich-Argent, R.I., Siedlewicz, G., Suarria, G., Tourgeli, M., 2021. Floating macro-litter leaked from Europe to the ocean. *Nat. Sustain.* 4 (5) <https://doi.org/10.1038/s41893-021-00722-6>.
- González-Ortegón, E., Laiz, I., Sánchez-Quiles, D., Cobelo-García, A., Tovar-Sánchez, A., 2019. Trace metal characterization and fluxes from the Guadiana, tinto-odiel and Guadalquivir estuaries to the Gulf of Cadiz. *Sci. Total Environ.* 650, 2454–2466.
- Hardesty, B.D., Harari, J., Isobe, A., Lebreton, L., Maximenko, N., Potemra, J., et al., 2017. Using numerical model simulations to improve the understanding of microplastic distribution and pathways in the marine environment. *Front. Mar. Sci.* 4, 30.
- Herberich, E., Sikorski, J., Hothorn, T., 2010. A robust procedure for comparing multiple means under heteroscedasticity in unbalanced designs. *PLoS One* 5 (3), e9788.
- Hitchcock, J.N., Mitrovic, S.M., 2019. Microplastic pollution in estuaries across a gradient of human impact. *Environ. Pollut.* 247, 457–466. <https://doi.org/10.1016/j.envpol.2019.01.069>.
- Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environ. Pollut.* 160, 42–48.
- Ivar do Sul, J.A., Costa, M.F., 2014. The present and future of microplastic pollution in the marine environment. *Environ. Pollut.* 185, 352–364.
- Kaminsky, W., 2013. In: *Polyolefins: 50 Years After Ziegler and Natta II: Polyolefins by Metalloenes and Other Single-Site Catalysts*, Vol. 258. Springer-Verlag, Berlin, p. 366.
- Kooi, M., Reisser, J., Slat, B., Ferrari, F.F., Schmid, M.S., Cunsolo, S., et al., 2016. The effect of particle properties on the depth profile of buoyant plastics in the ocean. *Sci. Rep.* 2016 (6), 33882.
- Kooi, M., Van Nes, E.H., Scheffer, M., Koelmans, A.A., 2017. Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics. *Environ. Sci. Technol.* 51, 7963–7971. <https://doi.org/10.1021/acs.est.6b04702>.
- Kooi, M., Koelmans, A.A., 2019. Simplifying microplastic via continuous probability distributions for size, shape, and density. *Environ. Sci. Technol. Lett.* 6 (9), 551–557.
- Kowalski, N., Reichardt, A.M., Waniek, J.J., 2016. Sinking rates of microplastics and potential implications of their alteration by physical, biological, and chemical factors. *Mar. Pollut. Bull.* 109, 310–319. <https://doi.org/10.1016/j.marpolbul.2016.05.064>.
- Laiz, I., Plecha, S., Teles-Machado, A., González-Ortegón, E., Sánchez-Quiles, D., Cobelo-García, A., et al., 2020. The role of the Gulf of Cadiz circulation in the redistribution of trace metals between the Atlantic Ocean and the Mediterranean Sea. *Sci. Total Environ.* 2020 (719), 134964.
- Lambert, S., Wagner, M., 2016. Characterisation of nanoplastics during the degradation of polystyrene. *Chemosphere* 145, 265–268.
- Law, K.L., Moret-Ferguson, S., Maximenko, N.A., Proskurowski, G., Peacock, E.E., Hafner, J., Reddy, C.M., 2010. Plastic accumulation in the North Atlantic subtropical gyre. *Science* 329, 1185e1188.
- Lebreton, L.C.M., Van der Zwet, J., Damsteeg, J.W., Slat, B., Andrady, A., Reisser, J., 2017. River plastic emissions to the world's oceans. *Nat. Commun.* 8, 15611.
- Lindeque, P.K., Cole, M., Coppock, R.L., Lewis, C.N., Miller, R.Z., Watts, A.J.R., Wilson-McNeal, A., Wright, S.L., Galloway, T.S., 2020. Are we underestimating microplastic abundance in the marine environment? A comparison of microplastic capture with nets of different mesh-size. *Environ. Pollut.* 265, 114721 <https://doi.org/10.1016/j.envpol.2020.114721>.
- Lopes, C., Raimundo, J., Caetano, M., Garrido, S., 2020. Microplastic ingestion and diet composition of planktivorous fish. *Limnol. Oceanogr. Lett.* 5 (1), 103–112.
- Lozano, L.R., Mouat, J., 2009. In: *Marine Litter in the North-East Atlantic Region*. OSPAR Commission, London, p. 127.
- McArde, B.H., Anderson, M.J., 2001. Fitting multivariate models to community data: a comment on distance-based redundancy analysis. *Ecology* 82 (1), 290–297.
- Miller, M.E., Kroon, F.J., Motti, C.A., 2017. Recovering microplastics from marine samples: a review of current practices. *Mar. Pollut. Bull.* 123, 6–18.
- Montoto-Martínez, T., Hernández-Brito, J.J., Gelado-Caballero, M.D., 2020. Pump-underway ship intake: an unexploited opportunity for marine strategy framework directive (MSFD) microplastic monitoring needs on coastal and oceanic waters. *PLoS One* 15 (5), e0232744.
- Murphy, J., 2001. In: *Additives for Plastics Handbook*, 2nd ed. Elsevier Advanced Technology, Oxford, p. 471.
- Pabortsava, K., Lampitt, R.S., 2020. High concentrations of plastic hidden beneath the surface of the Atlantic Ocean. *Nat. Commun.* 11 (1), 1–11.
- Pedrotti, M.L., Petit, S., Elineau, A., Bruzaud, S., Crebassa, J.C., Dumontet, B., et al., 2016. Changes in the floating plastic pollution of the Mediterranean Sea in relation to the distance to land. *PLoS One* 11 (8), e0161581.
- Peliz, A., Dubert, J., Marchesiello, P., Teles-Machado, A., 2007. Surface circulation in the Gulf of Cadiz: model and mean flow structure. *J. Geophys. Res. Oceans* 112. <https://doi.org/10.1029/2007JC004159>.
- Peliz, A., Marchesiello, P., Santos, A.M.P., Dubert, J., Teles-Machado, A., Marta-Almeida, M., Le Cann, B., 2009. Surface circulation in the Gulf of Cadiz: 2. Inflow-outflow coupling and the Gulf of Cadiz slope current. *J. Geophys. Res.* 114, C03011 <https://doi.org/10.1029/2008jc004771>.
- PlasticsEurope, 2020. *Plastics - the facts 2020*. URL. <https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020>.
- Poulain, M., Mercier, M.J., Brach, L., Martignac, M., Routabou, C., Perez, E., Desjean, M. C., Ter Halle, A., 2019. Small microplastics as a main contributor to plastic mass balance in the North Atlantic subtropical gyre. *Environ. Sci. Technol.* 53, 1157–1164. <https://doi.org/10.1021/acs.est.8b05458>.
- Prata, J.C., Silva, A.L.P., da Costa, J.P., Mouneyrac, C., Walker, T.R., Duarte, A.C., et al., 2019. Solutions and integrated strategies for the control and mitigation of plastic and microplastic pollution. *Int. J. Environ. Res. Public Health* 16 (13).

- Relvas, P., Barton, E.D., 2002. Mesoscale patterns in the Cape São Vicente (Iberian Peninsula) upwelling region. *J. Geophys. Res.* 107 <https://doi.org/10.1029/2000jc000456>.
- Schlitzer, R., 2002. Interactive analysis and visualization of geoscience data with ocean data view. *Comput. Geosci.* 28 (10), 1211–1218.
- Sendra, M., Staffieri, E., Yeste, M.P., Moreno-Garrido, I., Gatica, J.M., Corsi, I., Blasco, J., 2019a. Are the primary characteristics of polystyrene nanoplastics responsible for toxicity and ad/absorption in the marine diatom *Phaeodactylum tricornutum*? *Environ. Pollut.* 249, 610–619.
- Sendra, M., Sparaventi, E., Blasco, J., Moreno-Garrido, I., Araujo, C.V., 2020a. Ingestion and bioaccumulation of polystyrene nanoplastics and their effects on the microalgal feeding of *Artemia franciscana*. *Ecotoxicol. Environ. Saf.* 188, 109853.
- Sendra, M., Pereiro, P., Yeste, M.P., Mercado, L., Figueras, A., Novoa, B., 2020b. Size matters: zebrafish (*Danio rerio*) as a model to study toxicity of nanoplastics from cells to the whole organism. *Environ. Pollut.* 268, 115769.
- Sendra, M., Pereiro, P., Figueras, A., Novoa, B., 2021a. An integrative toxicogenomic analysis of plastic additives. *J. Hazard. Mater.* 409, 124975.
- Sendra, M., Sparaventi, E., Novoa, B., Figueras, A., 2021b. An overview of the internalization and effects of microplastics and nanoplastics as pollutants of emerging concern in bivalves. *Sci. Total Environ.* 753, 142024.
- Silva, A.B., Bastos, A.S., Justino, C.I.L., da Costa, J.A.P., Duarte, A.C., Rocha-Santos, T.A.P., 2018. Microplastics in the environment: challenges in analytical chemistry: a review. *Anal. Chim. Acta* 1017, 1–19.
- Sutton, R., Mason, S.A., Stanek, S.K., Willis-Norton, E., Wren, I.F., Box, C., 2016. Microplastic contamination in the San Francisco Bay, California, USA. *Mar. Pollut. Bull.* 109, 230–235. <https://doi.org/10.1016/j.marpolbul.2016.05.077>.
- Ter Halle, A., Jeanneau, L., Martignac, M., Jarde, E., Pedrono, B., Brach, L., et al., 2017. Nanoplastic in the North Atlantic subtropical gyre. *Environ. Sci. Technol.* 51 (23), 13689–13697.
- Vargas-Yáñez, M., Plaza, F., Garcia-Lafuente, J., Sarhan, T., Vargas, J.M., Velez-Belchi, P., et al., 2002. About the seasonal variability of the Alboran Sea circulation. *J. Mar. Syst.* 35 (3–4), 229–248.
- Vianello, A., Boldrin, A., Guerriero, P., Moschino, V., Rella, R., Sturaro, A., et al., 2013. Microplastic particles in sediments of lagoon of Venice, Italy: first observations on occurrence, spatial patterns and identification. *Estuar. Coast. Shelf Sci.* 130, 54–61.
- Wang, T., Li, B., Yu, W., Zou, X., 2021. Microplastic pollution and quantitative source apportionment in the Jiangsu coastal area, China. *Mar. Pollut. Bull.* 166, 112237 <https://doi.org/10.1016/j.marpolbul.2021.112237>.
- Walkinshaw, C., Lindeque, P.K., Thompson, R., Tolhurst, T., Cole, M., 2020. Microplastics and seafood: lower trophic organisms at highest risk of contamination. *Ecotoxicol. Environ. Saf.* 190, 110066 <https://doi.org/10.1016/j.ecoenv.2019.110066>.
- Wright, S.L., Rowe, D., Thompson, R.C., Galloway, T.S., 2013. Microplastic ingestion decreases energy reserves in marine worms. *Curr. Biol.* 23 (23), R1031–R1033.