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Occurrence of organic plastic additives in surface waters of the Rhône River (France)☆

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A B S T R A C T

We present here a comprehensive study (1-year regular sampling) on the occurrence of major families of organic plastic additives in the Rhône River surface waters. Potential sources and contaminant export are also discussed. A total of 22 dissolved phase samples were analyzed for 22 organic additives mainly used in the plastic industry, including organophosphate esters (OPEs), phthalates (PAEs) and bisphenols (BPs). Our results indicate that PAEs were the most abundant class, with concentrations ranging from 97 to 541 ng L^{-1}, followed by OPEs (85–265 ng L^{-1}) and BPs (4–21 ng L^{-1}). Among PAEs, diethylhexyl phthalate (DEHP) was the most abundant compound, whereas TCPP (Tris(1-chloro-2-propyl) phosphate) and TnBP (Tri(n-butyl)phosphate) were the predominant OPEs. Bisphenol S was the only BP detected. 5–54 metric tons $year^{-1}$ of dissolved organic plastic additives of emerging concern are estimated to be exported to the Gulf of Lion by the Rhône River, which is the main freshwater source of the Mediterranean Sea.

1. Introduction

Organic contaminants such as organophosphate esters (OPEs), phthalates (PAEs) and bisphenols (BPs) have been widely used in the last decade as additives in a broad range of products, such as detergents (PAEs), textiles (OPEs, PAEs), paints (OPEs, PAEs, BPs), food containers (PAEs, BPs) and plastics above all (OPEs, PAEs, BPs) (Hahladakis et al., 2018; Net et al., 2015b; Wei et al., 2015). These contaminants are commonly detected in marine and freshwater environments (Hermabessiere et al., 2017; Net et al., 2015b; Paluselli et al., 2018b; Pantelaki and Voutsa, 2019; Schmidt et al., 2019), and some of them have been classified or are suspected to act as endocrine disruptors (e.g., diethylhexyl phthalate, DEHP; tris(1-chloro-2-propyl) phosphate, TCPP). Even transgenerational effects have been shown to occur, e.g., through the exposure of mice to DEHP during pregnancy (Manikkam et al., 2013; Quinnies et al., 2017). However, Environmental Quality Standards (EQS) (i.e., maximum acceptable concentration thresholds in water, biota and sediments) have been derived (Directive 2008/105/EC) or proposed for only a few of them.

Rivers are known to be vectors for plastic debris (Horton et al., 2017; Schmidt et al., 2017), legacy contaminants such as polychlorinated biphenyls (PCBs) (Herrero et al., 2018) and contaminants considered of emerging concern, like PAEs (Paluselli et al., 2018a). Sánchez-Avila et al. (2012) concluded that rivers (along with wastewater treatment plants) are the main source of organic micropollutants, including BPs and PAEs, to the North Western Mediterranean coast. The knowledge of current environmental levels and fluxes is an important first step to identify contamination hot spots, estimate loadings to coastal areas and perform risk assessments. A limited number of studies have investigated the occurrence of OPEs in surface water from European rivers; for example, data exists for the Ruhr (Andresen et al., 2004), the Elbe (Wolschke et al., 2015) and the Danube rivers (Loos et al., 2017), whereas smaller datasets are available for others (Cristale et al., 2013; Fries and Püttmann, 2003; Martínez-Carballo et al., 2007). To our knowledge, no data considering OPEs in the Rhône River have been reported thus far. On the global scale, OPEs have extensively been studied in Chinese surface waters, e.g. in a study comprising 40 rivers where TCPP had a mean concentration of 186 ng L^{-1} (Wang et al., 2015). In five tributaries of the Lake Michigan (USA) TCPP had a mean concentration of 7.2–16 ng L^{-1} in

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water samples (Guo et al., 2017).

DEHP, generally the most abundant PAE in the environment, was detected at concentrations of 160–1700 ng L^{-1} in the Charmoise River, France (Tran et al., 2015), 540–920 ng L^{-1} in the Rhine River, the Netherlands (Peijnenburg and Struijs, 2006) and 0.79–3.63 μg L^{-1} in the Jiulong River, China (Li et al., 2017b). PAEs were previously analyzed in the Rhône River by Paluselli et al. (2018a, b), but only for one sampling date (March 2014; Σ_8 PAEs: 615 ng L^{-1}). Miège et al. (2012) measured bisphenol A (BPA) in fish samples from the Rhône River (mean BPA concentration of 13.7 ng g^{-1} dry weight), but no data for river water samples has been reported, neither concerning other bisphenols (such as bisphenol S), which are increasingly used to replace BPA (Wong et al., 2017).

The Rhône River, linking the Swiss Alps with the Mediterranean Sea, is 816 km long and is the main freshwater source of the NW Mediterranean Sea (Sempéré et al., 2000; Struglia et al., 2004). It has historically been of significant economic importance and has been highly modified by humankind (riverbed regulation, hydropower developments, etc.) over the course of time, passing through a heavily industrialized area with petrochemical industries and several nuclear plants. The Rhône River has already been studied on an annual basis for natural organic compounds, nutrients, dissolved inorganic carbon (DIC), chromophoric dissolved organic matter (CDOM), dicarboxylic acids, total suspended matter (TSM) fluxes and freshwater discharges (Coste and Raimbault, 1993; Panagiotopoulos et al., 2012; Para et al., 2010; Pont et al., 2002; Sempéré et al., 2018, 2000). In addition, recent studies showed that this river is a significant source of microplastics (Constant et al., 2018; Schmidt et al., 2018) and macroplastics (Castro-Jiménez et al., 2019) to the Mediterranean Sea. However, available data on anthropogenic organic compounds rely mostly on punctual or short-term measurements and focus mostly on classical organic contaminants like PCBs and Polycyclic Aromatic Hydrocarbons (PAHs) (Guigue et al., 2014; Mourier et al., 2014).

The objectives of this study were (i) to quantify OPEs, PAEs and BPs in water samples from the Rhône River during a one-year period, (ii) to identify possible sources and/or environmental drivers influencing contaminant concentrations and (iii) to provide a first estimate of fluxes into the NW Mediterranean Sea.

2. Materials and methods

2.1. Study area and sampling

One-liter surface water samples were collected monthly in duplicate (n = 22) from May 2017 to April 2018 (see Supplementary Material for sampling dates, water temperature and river flow rates). All samples were taken at arm-length from the dock in the Rhône River in Arles city (France) at 43.67858° N, 4.62073° E (Fig. 1) using precombusted (450 °C, 6 h) 1-L glass bottles. The samples were filtered through a glass fiber filter (GF/F, 0.7 μm) within 3 h after collection and were either stored at 4 °C in the dark and extracted within 24 h or otherwise stored at −25 °C in the dark (for three months max.) when immediate extraction was not possible. River water temperature was measured using a handheld electronic thermometer, and river flow data were extracted from the French "Banque Hydro" (http://www.hydro.eaufrance.fr/). The river flow data used originate from a measuring station (in the commune of Tarascon) approximately 16 km upstream of Arles. Just upstream of Arles, the river separates into the "Petit Rhône" (representing ~10% of the total water flow; Sempéré et al., 2000) and the "Grand Rhône". Since this division is downstream of the flow-measuring station, but upstream of the water sampling station, the river flow at the water sampling station was considered to correspond to approximately 90% of the flow measured in Tarascon. The daily river flow during the whole sampling period is shown in Fig. S1 A. All six wastewater treatment plants (WWTPs) situated in the commune of Arles are located downstream of our sampling station. However, about 15 km upstream of the sampling station, the WWTP effluents from Tarascon (17,583 inhabitant equivalent) and Beaucaire (29,246 inhabitant equivalent) enter the Rhône River.

2.2. Solvents and chemical standards

Solvents were purchased from Biosolve (ULC-MS grade methanol) and Promochem (Picograde, LGC n-hexane, ethyl acetate and dichloromethane). Isotope-labeled and native bisphenols were obtained from AccuStandard (USA); labeled and native phthalates from Supelco (USA). Isotope-labeled OPEs were purchased from C/D/N Isotopes Inc. (Canada) (D_{27}-Tri-n-butyl phosphate -D_{27}-TBP-, D_{15}-Triphenyl phosphate -D_{15}-TPhP-, D_{21}-Tri-n-propyl phosphate -D_{21}-TPrP- and D_7Malathion -D_7-MAL-) and from Cambridge Isotope Laboratories, Inc. (USA) (D_{18}-Tris(1-chloro-2-propyl) phosphate -D_{18}-TCPP-, D_{15}-Tris (1,3-dichloro-2-propyl) phosphate -D_{15}-TDCP- and D_{12}-Tris (2-chloroethyl) phosphate -D_{12}-TCEP-). Native OPEs were obtained from Dr. Ehrenstorfer GmbH (Germany). CAS numbers of all compounds, as well as their monoisotopic masses and log K_{ow} values are given in Supplementary Material (Table S1).

2.3. Sample processing and analysis

Solid phase extraction (SPE) was carried out following a protocol described elsewhere (Fauvelle et al., 2018). Briefly, after filtration (GF/F, 0.7 μm) and the addition of labeled surrogate standards for the three organic classes (100 ng $sample^{-1}$ of D_{27}-TBP, D_{18}-TCPP, D_{15}-TDCP, D_{15}-TPhP and D_4-di-n-butyl phthalate -D_4-DnBP- and 20 ng $sample^{-1}$ of 4-n-octylphenol-D_{17} -4nOP-D_{17}-), the water was passed through precombusted and precleaned glass cartridges containing 250 mg SPE sorbent (Oasis hydrophilic lipophilic balance HLB, Waters, Guyancourt, France) *via* polytetrafluoroethylene (PTFE) liners. Next, the cartridges were vacuum-dried for 2–3 h to complete dryness.

Molecules of interest were then sequentially eluted using a solvent polarity gradient resulting in two different fractions by using 5 mL of n-hexane followed by 5 mL of n-hexane/dichloromethane 50:50 (v/v) for PAEs and OPEs (F_a fraction) and 5 mL of ethyl acetate followed by 5 mL of methanol for BPs (F_b fraction). The extracts were then evaporated using pure N_2 gas until a volume of approximately 1 mL was transferred into 2-mL conical glass vials. The extracts were further concentrated through gentle N_2 flux to (F_a) a final volume of approximately 100 μL or (F_b) dryness in which case the extract was then reconstituted with 990 μL of methanol. Internal standards for quantification were then added as follows: (F_a) 100 ng $sample^{-1}$ of D_4-diethyl phthalate (D_4-DEP), D_4-diethylhexyl phthalate (D_4-DEHP), D_{21}-TPrP, D_{12}-TCEP and D_7-MAL and (F_b) 20 ng $sample^{-1}$ of D_{16}-bisphenol A (D_{16}-BPA) (Table S2).

For PAEs and OPEs, F_a was injected into a gas chromatograph coupled with a mass spectrometry detector (GC-MS, Agilent 7820A Series GC – Agilent 5977E MS) for the quantification of nine organophosphate esters (tripropyl phosphate -TPP-, tri-iso-buthyl phosphate -TiBP-, tri-n-butyl phosphate -TnBP-, tris-(2-chloroethyl) phosphate -TCEP-, tris-(2-chloro, 1-methylethyl) phosphate -TCPP-, tris-(2-chloro-, 1-chloromethylethyl) phosphate -TDCP-, triphenyl phosphate -TPhP-, 2-ethylhexyl-diphenyl phosphate -EHDPP- and tris(2-ethylhexyl) phosphate -TEHP-) and seven phthalates (dimethyl phthalate -DMP-, diethyl phthalate -DEP-, diisobutyl phthalate -DiBP-, di-n-butyl phthalate -DnBP-,

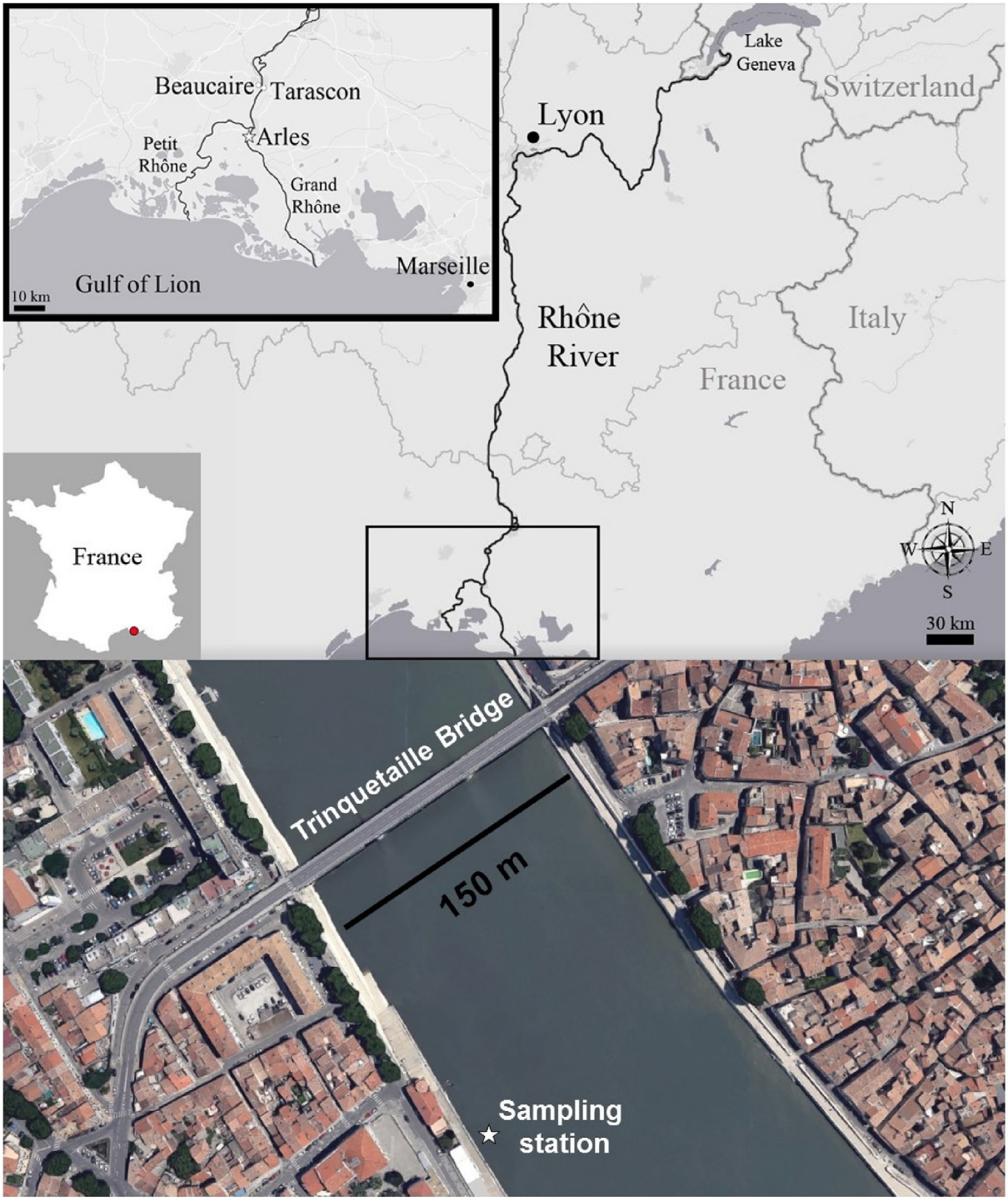


Fig. 1. Map showing the French part of the Rhône River after leaving Lake Geneva until its estuary in the Gulf of Lion (NW Mediterranean Sea). A zoomed image in the left corner shows the position of the river discharge measuring station at Tarascon, the water sampling station (star) in Arles and the two river branches "Petit Rhône" (left) and "Grand Rhône" (right) representing ~10% and 90% of the total water flow, respectively. At the bottom an aerial view indicates the position of the sampling station.

benzylbutyl phthalate -BzBP-, diethylhexyl phthalate -DEHP- and di-n-octyl phthalate -DnOP-); while for the quantification of six bisphenols (bisphenol A -BPA-, bisphenol AF -BPAF-, bisphenol AP -BPAP-, bisphenol F -BPF-, bisphenol S -BPS- and bisphenol Z -BPZ-) F_b was injected into a liquid chromatograph coupled to a high-resolution time-of-flight mass spectrometer *via* an electrospray ionization interface (LC-ESI-QTOF, Agilent 1290 Infinity LC system coupled with Agilent 6530 Accurate-Mass Q-TOF). All details on GC-MS and LC-ESI-QTOF analyses can be found in the Supplementary Material (Text S1).

Dissolved organic carbon (DOC) was measured from filtered (GF/F, 0.7 μm), acidified (by 20 μL of 85% H_3PO_4 acid) Rhône River water subsamples using a Shimadzu TOC-5000 carbon analyzer (Sempéré et al., 2008). The instrument blank (≤5 μM) was subtracted from all measured data. GF/F filters were acidified with 50 μL H_2SO_4 (0.5 N) to remove inorganic carbon and analyzed for particulate organic

carbon (POC) and nitrogen (PON) using high combustion (1000 °C) on a CN Integra mass spectrometer (SERCON), calibrated using glycine references for every batch of 10–15 samples (Raimbault et al., 2008).

2.4. Quality assurance/quality control

The extractions were carried out in an ISO class 6 cleanroom equipped for organic trace analysis. All glassware used was carefully cleaned, rinsed with demineralized and ultrapure water and burned at 450 °C for 6 h. All plastic material was avoided during sampling, extraction and analysis. All organic contaminants and DOC analyses were performed in duplicate. Surrogate recoveries ranged from 83 to 119% (D_4-DnBP), 85–102% (D_{27}-TBP), 68–96% (D_{18}-TCPP), 83–104% (D_{15}-TDCP), 72–95% (D_{15}-TPhP) and 64–79% (4nOP-D_{17}). Native spike experiments performed in a previous study in order to evaluate method recoveries of native compounds also showed good method recoveries, ranging from 61 ± 4 to 131 ± 5% for OPEs, from 52 ± 3 to 89 ± 1% for PAEs and from 79 ± 4 to 118 ± 26% for BPs (Fauvelle et al., 2018). Extraction in batches was considered as producing lower bias in reproducibility due to solvents, standards, handling and instrument functioning. Duplicate extraction blanks were made for each extraction batch (containing 6–8 duplicate samples) to detect potential contaminations which could occur during the sensible steps of sample extraction, processing and analysis. Samples were blank corrected by subtracting the averaged blank value of the specific batch. No particular blank issues were detected. PAE concentrations in blanks were as follows: DEP n.d.-2.0 ng L^{-1}, DiBP 1.8–5.0 ng L^{-1}, DnBP n.d.-2.9 ng L^{-1} and DEHP 7.0–37.0 ng L^{-1}. DMP, BzBP and DnOP were not detected in blanks. OPEs were detected in blanks at levels lower than the limits of quantification (LOQs) (TiBP, TnBP and EHDPP), not detected at all (TPP, TCEP, TDCP, TPhP and TEHP) or, in the case of TCPP, were detected at constantly low concentrations of 3.6–4.0 ng L^{-1}. BPs were either not detected in blanks or were present at low concentrations (n.d.-0.1 ng L^{-1} for BPS, n.d.-6.7 ng L^{-1} for BPZ). Method LOQs ranged from 0.03 to 0.75 ng L^{-1} for OPEs, from 0.03 to 0.25 ng L^{-1} for PAEs and from 0.1 to 5.0 ng L^{-1} for BPs (Table S3). The average DOC concentration measured in the Deep Seawater reference material (batch 17, lot# 04–17; D. Hansell, Rosenstiel School of Marine and Atmospheric Science, Miami, USA) was 45 ± 1 μM C (n = 8).

2.5. Data processing

Correlations between PAEs, OPEs, BPs, DOC, POC, PON and river discharge were assessed through a correlation matrix using linear correlation coefficients. Correlations were considered strong if the correlation coefficient was ≥ ± 0.7. To perform a rough estimation of the dissolved organic additive inputs of the Rhône River to the NW Mediterranean Sea contaminant fluxes were estimated. For this, the concentrations measured at each sampling day was multiplied with the corresponding daily river flow. The daily river flows are presented in Table 1.

3. Results and discussion

River discharge varied on sampling days between 460 and 3960 m^3 s^{-1}, water temperature between 5 and 25 °C and DOC concentrations between 80 and 164 μM (average 127 ± 26 μM or 1517 ± 315 μg L^{-1}) (Table 1, Fig. 2A). These values are in line with DOC concentrations measured at the same sampling station between 2006 and 2009 (80–216 μM; Sempéré et al., 2018) and with those reported by Panagiotopoulos et al. (2012) (average 134 μM). POC and PON ranged from 185 to 2134 μg L^{-1} and from 47 to 303 μg L^{-1}, respectively. More importantly, they followed the same dynamic as the river discharge (Fig. 2A) and were thus positively correlated with it ($p < 0.01$). Our average POC concentration (667 μg L^{-1}) is notably lower than the one observed by Panagiotopoulos et al. (2012) (3096 μg L^{-1}), and in their study, a correlation between POC concentrations and river discharge could not be observed, probably due to incoherent POC dynamics during flood events.

3.1. Concentration levels and relative abundances

PAEs, OPEs and BPs were, for the first time, simultaneously measured in the Rhône River on a monthly basis. PAEs were the compound class reaching the highest concentrations compared to the other two contaminant families (97–541 ng L^{-1}; av. relative abundance 64% ± 10% standard deviation SD) followed by OPEs (85–265 ng L^{-1}; av. relative abundance 34% ± 10% SD) and BPs (4–21 ng L^{-1}; av. relative abundance 2% ± 1% SD), except in April 2018 when OPEs were predominant with ~52% relative abundance (Table S4, Table 2). Hereby, the predominance of OPEs in April 2018 is mainly due to the lowest PAE concentration measured throughout the study. Overall, the highest plastic additive concentrations in surface water from the Rhône River were measured in September 2017, with ~830 ng L^{-1} for $\sum_{17}$ compounds detected.

3.1.1. Phthalates

The highest $\sum_7$ PAE levels were found in the months of May, September and December 2017 (Fig. 2B), with values in the range of

Table 1
Sampling time and date, water temperature (°C), dissolved organic carbon (μM) and river discharge (m^3 s^{-1}). River discharge data were extracted from "Hydro Banque" (http://www.hydro.eaufrance.fr) from their measuring station at Tarascon, approximately 16 km upstream of our sampling station. Since the Rhône River separates into two branches (Petit Rhône and Grand Rhône) after the discharge measuring station, we estimated that the flow rate at our sampling station amounted to approximately 90% of the original value.

Date	Time of day	Water temperature (°C)	DOC (μM)	Approx. discharge rate (m^3 s^{-1})
05/23/2017	09:00	18.3	114	1116
06/22/2017	10:24	24.6	80	785
08/24/2017	11:38	23.5	117	470
09/19/2017	08:39	20.9	100	626
11/03/2017	09:08	14.0	118	460
11/30/2017	10:53	9.4	134	1026
12/12/2017	10:13	8.2	164	2772
01/05/2018	10:11	8.6	162	3960
02/13/2018	12:04	7.3	145	1521
03/01/2018	10:46	5.0	n.a.	1566
04/09/2018	12:57	11.7	131	2340

n.a. = not available.

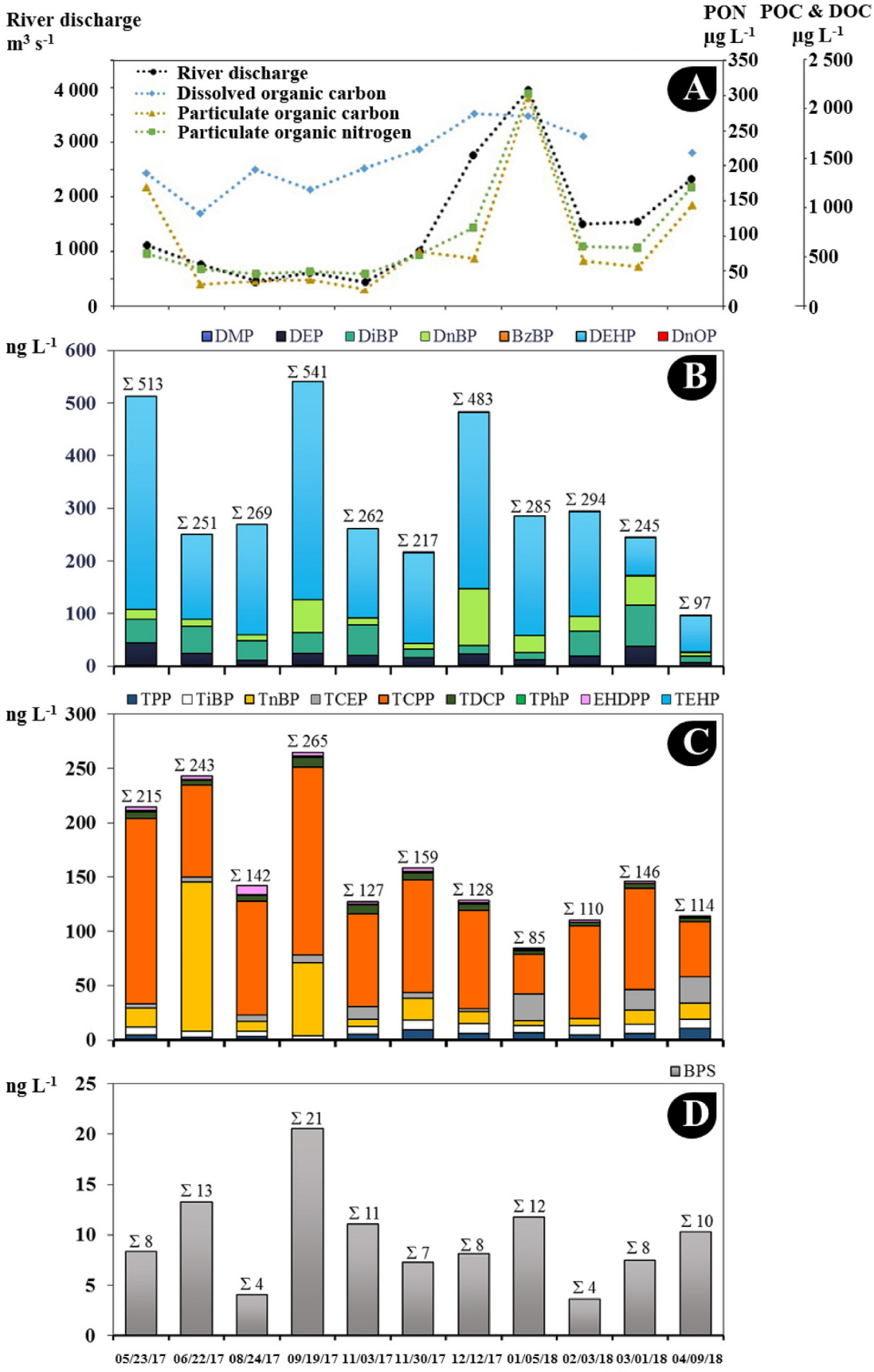


Fig. 2. (A) River discharge ($m^3\ s^{-1}$), PON ($\mu g\ L^{-1}$), POC ($\mu g\ L^{-1}$) and DOC ($\mu g\ L^{-1}$) concentrations measured during the sampling events, (B) concentrations (in $ng\ L^{-1}$) of the seven phthalates, (C) nine organophosphate esters and (D) six bisphenols. BPS was the only bisphenol detected. The March DOC sample was excluded due to contamination issues. Σ means sum of the concentrations of all individual molecules within each class of compounds. The dotted lines in (A) are there to facilitate the reading of the graph, but do not indicate an extrapolation between individual measurements.

Table 2
Descriptive statistic of detected compounds. Concentrations are given in ng L^{-1}.

	TPP	TiBP	TnBP	TCEP	TCPP	TDCP	TPhP	EHDPP	Σ OPEs	DMP	DEP	DiBP	DnBP	BzBP	DEHP	DNOP	Σ PAEs	BPS
Min.	n.d.	3.8	4.4	n.d.	36.6	3.1	n.d.	1.3	84.8	0.8	6.9	11.1	7.3	n.d.	69.6	n.d.	97.0	3.7
Max.	10.7	9.3	138.1	25.0	173.1	8.7	1.4	8.0	264.6	2.4	42.1	78.2	107.7	0.6	414.4	0.9	540.8	20.5
Median	5.6	7.3	12.9	6.1	90.5	5.4	1.1	1.9	142.0	1.5	19.3	39.7	19.0	0.5	198.3	0.8	269.4	8.4
Mean	5.9	7.1	28.0	10.8	98.2	5.4	1.1	2.8	157.5	1.5	20.6	37.3	32.8	0.5	221.4	0.8	314.2	9.6
SD	3.0	2.0	40.5	8.9	42.1	1.9	0.5	1.9	58.0	0.5	10.7	21.6	31.0	0.1	117.5	0.4	138.0	4.7

those reported by Paluselli et al. (2018a, b) (615 ng L^{-1}, $\sum_7$ PAEs) for March 2014 at the same sampling site. DEHP, generally the most abundant PAE, was found at concentrations ranging from 70 to 405 ng L^{-1} (mean 221 ng L^{-1}). Previous studies in French water courses reported higher concentrations in three rivers in the Parisian area (average 323–779 ng L^{-1} DEHP; Teil et al., 2007) and in several French-Belgian transboundary rivers (0.8–126 μg L^{-1} DEHP; Net et al., 2015a). Domínguez-Morueco et al. (2014) did not detect DEHP in any river or tap water samples from Spain and attributed this condition to the existing regulations restricting the use of DEHP for certain products (e.g., plastic toys). However, their LOD (460 ng L^{-1}) and LOQ (970 ng L^{-1}) values were quite elevated and they may have missed trace level concentrations.

Branched chain PAEs, including DEHP and DiBP, were found to be the most abundant PAEs, with DEHP being predominant with its relative abundance varying between 29.5 and 79.6% (mean 69%) of total PAEs, which is in line with the 66% and 54% relative DEHP abundance reported by Paluselli et al. (2018a, b) and Net et al. (2015a), respectively. DMP, BzBP and DnOP were only detected at low concentrations (≤2.5 ng L^{-1}) or were not detected at all. DEP abundance varied between 3.6 and 14.7% of Σ_7 PAEs, whereas DiBP and DnBP relative abundances were between 3.2–31.9% and 3.7–22.6%, respectively (Table S4). Interestingly, the sample collected in March (03/01/2018) exhibited a different pattern, with a remarkably low DEHP relative abundance (29.5%) compared to the other months (64.7–79.6%) and with higher DEP and DiBP percentages (Fig. 2B, Table S4). A possible explanation could be the rainfall (3.2 mm) observed on this given day, representing the only real rain event during the sampling days (daily precipitation data for the whole study period is shown in Figure S1 B). Previous works indicated that DEHP is less abundant in rainwater compared to other PAEs, possibly due to the short half-life of DEHP in the atmosphere (Fernández-Amado et al., 2017; Teil et al., 2006). This could possibly explain our observation; however, our present dataset is too limited to draw valid conclusions on this matter. Higher sampling frequencies and a detailed investigation of the particulate-dissolved partitioning of PAEs, particularly DEHP, would be needed.

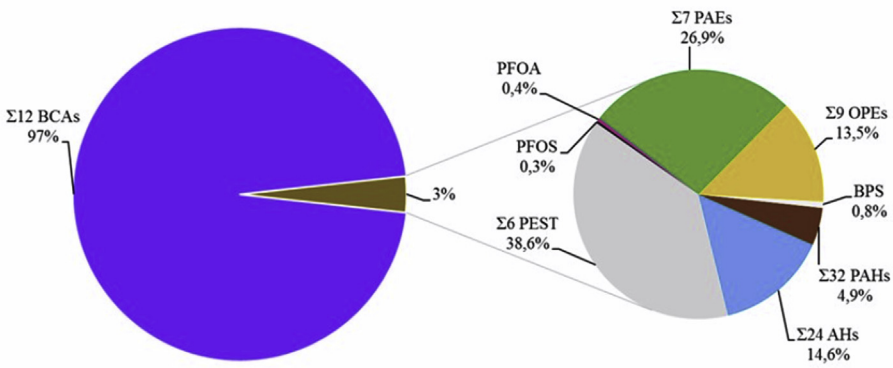
WWTP effluents are major PAE sources to rivers and previous studies have reported that the relative abundances of individual PAEs depended on the effluent type. For example, industrial laundries were shown to be the main DEHP and DEP source in industrial effluents, while DnBP was mostly associated with the pharmaceutical industry (Bergé et al., 2014). Concerning domestic effluents, dishwater graywater was reported as an important DnBP source (54% relative abundance), while DEHP was predominant in all other types of graywater (Deshayes et al., 2017). In the case of our sampling station, two WWTPs are situated ~15 km upstream and are probable sources of the organic contaminants measured in this study, as well as the plastic packaging and plastic material industry located in the commune of Avignon (~35 km upstream). Furthermore, direct leaching from floating plastic debris present in the watercourse could contribute to the PAE, and other plastic additive, stocks in surface waters (León et al., 2018; Paluselli et al., 2019). Recent studies reported the widespread presence of macro- and microplastics in surface waters of the Rhône River (Castro-Jiménez et al., 2019; Constant et al., 2018; Schmidt et al., 2018).

3.1.2. Organophosphate esters

Total OPE concentrations were generally slightly lower than total PAE concentrations. They reached a maximum in September 2017, while the lowest concentration was measured in January 2018 (Fig. 2C). Highest Σ_9 OPEs concentrations were found when water temperature was highest (May–September, 18.3–24.6 °C; Table 1), suggesting that temporal variability may depend on water temperature to a certain extent (see section 3.2). TCPP was predominant in this study, with concentrations of 37–173 ng L^{-1} (mean 98 ng L^{-1}). Such TCPP concentration levels are in the lower range of those previously reported in other rivers: 126 ± 14 ng L^{-1} in the Elbe River (Germany) (Wolschke et al., 2015), and 28–603 ng L^{-1} in the Danube River (Loos et al., 2017). In 40 rivers in China TCPP was the most abundant OPE, with concentrations of 5–921 ng L^{-1} (Wang et al., 2015). TCPP was also the most abundant OPE in this study (av. relative abundance 62% ± 15% SD), followed by TnBP (av. relative abundance 14% ± 15% SD) and TCEP (av. relative abundance 9% ± 10% SD) (Table S4). Interestingly, the sample collected in June 2017 exhibited a different pattern, with a much higher TnBP relative abundance (56.8%) compared to the rest of the samples (4.8–25.5%) and the lowest TCPP abundance (34.9%) of the sample period (Fig. 2C, Table S4). Overall, TnBP concentrations varied between 4 and 138 ng L^{-1}. TnBP is used as a plasticizer, corrosion inhibitor and antifoaming agent, among other things. It is also used in the nuclear industry to reprocess spent fuel by a process called PUREX (Revathi et al., 2014). Note that nuclear power is the main energy source in France and the Rhône watershed has the highest concentration of nuclear power plants in Europe. Furthermore, the Rhône River accommodates an ancient nuclear fuel reprocessing plant (Olivier et al., 2009), which could thus be a TnBP source. The fluctuating abundance of TnBP (including its high abundance in the June 2017 sample) could therefore be linked to varying inputs from the nuclear industry, though other sources cannot be excluded and a dedicated study should investigate these inputs. TEHP was not detected in water samples from this campaign (see Fig. S2 for detection frequencies). This was expected since TEHP tends to concentrate in sediments instead of in the dissolved water phase (Liu et al., 2018).

3.1.3. Bisphenols

Of the six different BPs screened for, only BPS was detected in our samples. The concentrations ranged between 4 and 21 ng L^{-1}, with a mean of 10 ng L^{-1} (Fig. 2D, Table 2). These values are comparable to those of other studies investigating BPs in river water (Jin and Zhu, 2016; Yamazaki et al., 2015). The highest concentration was found on September 19th, 2017, as was the case for Σ PAEs and Σ OPEs (Fig. 2). While BPS can be used as a substitute for BPA in certain products (e.g., as a color developer in thermal paper or as an additive in polycarbonate plastics), BPA still dominates these sectors (Björnsdotter et al., 2017; Pivnenko et al., 2018) and a higher BPA than BPS concentration could thus probably be expected in the environment. Therefore, it is remarkable that we did not detect any



Abbreviation	*Full name*	*Reference*
BCAs	Bi-functional carboxylic acids	Sempéré et al., 2018
PAHs	Polycyclic aromatic hydrocarbons	Guigue et al., 2014
AHs	Aliphatic hydrocarbons	Guigue et al., 2014
PEST	Pesticides & metabolites	Slomberg et al., 2017
PFOS	Perfluorooctane sulfonate	Munoz et al., 2015
PFOA	Perfluorooctanoic acid	Munoz et al., 2015
PAEs	Phthalates	This study
OPEs	Organophosphate esters	This study
BPS	Bisphenol S	This study

Fig. 3. Relative abundance (in %) of dissolved organic compounds in Rhône River surface waters (Munoz et al., 2015 and Slomberg et al., 2017).

BPA in our samples. However, it is noteworthy that BPA is rapidly degraded in river water under aerobic conditions (e.g., 1000 ng mL^{-1} can be reduced to < 0.5 ng mL^{-1} in seven days; Kang and Kondo, 2005), while BPS is significantly less biodegradable (Danzl et al., 2009; Ike et al., 2006). This could explain the lack of BPA in our samples, but other reasons cannot be excluded (e.g., differences in physicochemical properties or sorption behavior).

3.1.4. Relative importance of PAEs, OPEs and BPs in the Rhône River

A comparison with available scientific literature was made to assess the relative importance of PAE, OPE and BP concentrations compared to other anthropogenic dissolved organic compounds in the Rhône River (Fig. 3). Using average concentrations, it was observed that bi-functional carboxylic acids (BCAs) represent 97% of dissolved organic compounds present in surface waters of the Rhône River. While BCAs in aquatic systems are not considered as typical contaminants, they can be generated from the incomplete combustion of fossil fuels, biomass burning and photooxidation of precursor organic compounds (Sempéré et al., 2018 and references therein) and their relative origin (natural versus anthropogenic) is not perfectly established in the aquatic ecosystem. The remaining 3% of organic compounds are mainly made up by pesticides and pesticide metabolites (PEST; 38.6%), PAEs (26.9%), aliphatic hydrocarbons (AHs; 14.6%), OPEs (13.5%) and polycyclic aromatic hydrocarbons (PAHs; 4.9%). BPS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are minor contributors (<1% each).

3.2. Variability, fluxes and potential sources to the Rhône River and the Mediterranean Sea

The highest contaminant concentrations observed in September 2017 do not correspond to the highest river discharge, nor to the maximum or minimum DOC, POC or PON concentrations. Actually, the September sample corresponded to one of the lowest river discharge values and to the higher values of water temperature registered during the sampling period. Temperature is known to be a key factor affecting the dissolved-particulate partition of semi-volatile organic contaminants (Berrojalbiz et al., 2011). Higher water temperatures could have favored the partitioning of some of the organic additives towards the dissolved water phase, but since the particulate phase was not analyzed in this study, we cannot evaluate this. Furthermore, this situation was not observed for the months of June and August, which also had conditions of high temperature and low water discharge, suggesting that other factors (e.g., changes in emission sources, precipitation or water flow) are probably more important drivers. Moreover, high water temperatures are rather expected to stimulate PAE biodegradation processes (by increasing bacterial activity), and thus to lower PAE concentrations (Net et al., 2015a). High PAE concentrations observed in September, June and December (541, 513 and 483 ng L^{-1}, respectively) might also be due to peaks in plastic concentrations that may release PAEs into surrounding waters (Paluselli et al., 2019).

A correlation matrix (Table S5) confirmed the correlation between river discharge and POC and PON. Furthermore, DOC was positively correlated with river discharge and negatively correlated with water temperature. ΣOPEs was negatively correlated with DOC and positively correlated with water temperature. For ΣPAEs and BPS, no such correlation was observed, indicating that the three contaminant families are not influenced in the same manner by environmental drivers, such as temperature and DOC. When examining individual contaminants, TiBP was negatively correlated with water temperature. Water temperature could potentially be considered a proxy for seasonality, including primary production, UV intensity and recreational activities. Moreover, several individual contaminants were positively correlated (TCPP with DMP and DEHP, TPhP with DEHP, DMP with DEHP and DiBP with DnOP), indicating that they follow the same dynamics but are not necessarily (or not exclusively) forced by river discharge, water temperature or carbon and nitrogen concentrations in the water column. Most likely, a combination of various factors (including phenomena such as biotransformation and photolytic transformation, which were not investigated in this study) as well as varying contaminant inputs resulted in the temporal variability observed. No significant correlation (p-value > 0.05) between mean concentrations of target compounds and their corresponding log K_{ow} value was observed.

We calculated daily fluxes of 10–116 kg, 5–31 kg and of 0.2–4 kg for PAEs, OPEs and BPS, respectively. Finally, using the same calculation method for all organic contaminants combined (Σ OPEs + Σ PAEs + Σ BPs), we achieved a daily flux of 15–149 kg. Table S6 summarizes the estimated fluxes. Assuming that this range of daily contaminant flux is representative for the whole year, an annual input ranging from 5 to 54 t of plastic additives is expected from the Rhône River to the Gulf of Lion in the NW Mediterranean Sea. Such kind of calculations have an important uncertainty associated with the large variation of contaminant concentrations depending on the pollution source (sporadic *vs.* chronic pollution) and environmental factors such as river flow (see section 3.2.), rain, UV radiation, temperature or pH (Li et al., 2017a; Noyes et al., 2009). Furthermore, the contaminants associated with the particle water phase were not measured in our study, most likely leading to an underestimation of total contaminant fluxes, especially regarding

hydrophobic substances.

Plastic debris can be a source of organic plastic additives through leaching (Net et al., 2015b). Recent estimations based on field observations of floating macro- and microplastics in the Rhône River suggested plastic fluxes of 0.71 t year^{-1} and 0.07–7.8 t year^{-1}, respectively (Castro-Jiménez et al., 2019; Schmidt et al., 2018). Both studies focused on the observation of floating plastic debris only and included a limited amount of samples, but suggest that the additive concentrations in the dissolved water phase cannot be entirely explained by the leaching from floating plastic waste. Furthermore, a recent experimental study points to low PAE release rates from plastic materials (e.g., ~120 ng DnBP g^{-1} plastic bag after 4 weeks in dark, biotic conditions, Paluselli et al. (2019)), supporting this hypothesis, even though seawater was used in this study and similar experiments with riverine water remain yet to be done. However, non-floating plastic can also contribute to this "leaching source" and increasing evidence suggests that this non-floating plastic burden is potentially more important than so far assumed (Karlsson et al., 2018; Van Sebille et al., 2015). In addition, other possible sources of contaminants to the Rhône River include inputs during the manufacturing of plastic materials, graywater and effluents from WWTPs and atmospheric deposition.

For the Mediterranean Sea, other important rivers, such as the Nile and Po rivers, could furthermore constitute important organic contaminant sources, alongside with highly inhabited and/or industrialized cities. Furthermore, atmospheric deposition has been confirmed as an efficient input pathway for OPEs in the Mediterranean Sea (Castro-Jiménez et al., 2014) and also in other marine environments (Castro-Jiménez et al., 2016). There are no available data from the atmospheric inputs of OPEs close to the Rhône area; however, recent estimations performed in another coastal site in the Western Mediterranean Sea point to dry deposition fluxes ranging from 18 to 180 ng m^{-2} d^{-1} for $\sum_9$ OPEs (Castro-Jiménez et al., 2018). If we consider these fluxes to be representative of Western Mediterranean coastal areas and extrapolate them to the whole Gulf of Lion (1.6×10^{10} m^2; Alekseenko et al., 2014), 0.1 to 1.1 t y^{-1} of OPEs (median value of 0.5 t y^{-1}) could be loaded from the atmosphere to the Gulf of Lion *via* dry deposition. However, a more representative assessment of the atmospheric inputs of plastic additives in the Gulf of Lion area, also including air-sea gas exchanges, is needed to constraint the uncertainty.

4. Conclusions

PAEs, OPEs and BPs were measured in dissolved phase surface waters from the Rhône River and detected in all samples, with DEHP and TCPP being the most abundant compounds. Temporal variability in contaminant concentrations, which was not clearly linked to river discharge or other bulk parameters, were observed. A combination of sources such as WWTPs, leaching from plastic debris, atmospheric deposition and the nuclear industry would most probably explain the occurrence of these organic contaminants in surface waters of the Rhône River. Rough flux estimations indicated that the Rhône River could be an important source of organic plastic additives *via* dissolved water phase transport to the NW Mediterranean Sea, which could certainly contribute to the contaminant cocktail potentially affecting the local food web, at least in the vicinity of the Rhône River mouth. However, data from other important rivers entering the Mediterranean Sea are needed for comparison. To the best of our knowledge, these are the first measurements of OPEs and BPS in the Rhône River, the main freshwater supplier of the Mediterranean Sea. Given the semi-enclosed nature of the Mediterranean Sea, the high anthropogenic pressure it receives and the scarcity of water resources in the Mediterranean, high contaminant fluxes *via* freshwater inputs could have more severe impacts on the ecosystem than they would have in the case of the global ocean.

Declaration of competing interest

The authors have no conflicts of interest to declare. The funding sources had no involvement in the collection, analysis and interpretation of data; in the writing of the report; and in the decision to submit the article for publication.

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References

Alekseenko, E., Raybaud, V., Espinasse, B., Carlotti, F., Queguiner, B., Thouvenin, B., Garreau, P., Baklouti, M., 2014. Seasonal dynamics and stoichiometry of the planktonic community in the Northwestern Mediterranean Sea: a 3D modeling approach. Ocean Dyn. 64, 179–207.

Andresen, J.A., Grundmann, A., Bester, K., 2004. Organophosphorus flame retardants and plasticisers in surface waters. Sci. Total Environ. 332, 155–166. https://doi.org/10.1016/j.scitotenv.2004.04.021.

Bergé, A., Gasperi, J., Rocher, V., Gras, L., Coursimault, A., Moilleron, R., 2014. Phthalates and alkylphenols in industrial and domestic effluents: case of Paris conurbation (France). Sci. Total Environ. 488–489, 26–35. https://doi.org/10.1016/j.scitotenv.2014.04.081.

Berrojalbiz, N., Dachs, J., Ojeda, M.J., Valle, M.C., Castro-Jiménez, J., Wollgast, J., Ghiani, M., Hanke, G., Zaldivar, J.M., 2011. Biogeochemical and physical controls on concentrations of polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black Seas. Glob. Biogeochem. Cycles 25, 1–14. https://doi.org/10.1029/2010GB003775.

Björnsdotter, M.K., Jonker, W., Legradi, J., Kool, J., Ballesteros-Gómez, A., 2017. Bisphenol A alternatives in thermal paper from The Netherlands, Spain, Sweden and Norway. Screening and potential toxicity. Sci. Total Environ. 601–602, 210–221. https://doi.org/10.1016/j.scitotenv.2017.05.171.

Castro-Jiménez, J., Barhoumi, B., Tedetti, M., Sempéré, R., 2018. Atmospheric particle-bound organophosphate ester flame retardants and plasticizers in a North African Mediterranean coastal city (Bizerte, Tunisia). Sci. Total Environ. 642, 383–393. https://doi.org/10.1016/j.scitotenv.2018.06.010.

Castro-Jiménez, J., Berrojalbiz, N., Pizarro, M., Dachs, J., 2014. Organophosphate ester (OPE) flame retardants and plasticizers in the open mediterranean and black seas atmosphere. Environ. Sci. Technol. 48, 3203–3209. https://doi.org/10.1021/es405337g.

Castro-Jiménez, J., Casal, P., González-Gaya, B., Pizarro, M., Dachs, J., 2016. Organophosphate ester flame retardants and plasticizers in the global oceanic atmosphere. Environ. Sci. Technol. 50, 12831–12839.

Castro-Jiménez, J., González-Fernández, D., Fornier, M., Schmidt, N., Sempéré, R., 2019. Macro-litter in surface waters from the rhone river: plastic pollution and flows to the NW Mediterranean Sea. Mar. Pollut. Bull. 146, 60–66. https://doi.org/10.1016/j.marpolbul.2019.05.067.

Constant, M., Kerhervé, P., Sola, J., Sanchez-Vidal, A., Canals, M., Heussner, S., 2018. Floating microplastics in the northwestern Mediterranean Sea: temporal and spatial heterogeneities. In: Proceedings of the International Conference on Microplastic Pollution in the Mediterranean Sea. Springer International Publishing, pp. 9–15. https://doi.org/10.1007/978-3-319-71279-6.

Coste, B., Raimbault, P., 1993. Recent data on the nutrient input into the Mediterranean Sea by the Rhône river. Water Res. 30, 47–50.

Cristale, J., García Vázquez, A., Barata, C., Lacorte, S., 2013. Priority and emerging flame retardants in rivers: occurrence in water and sediment, Daphnia magna toxicity and risk assessment. Environ. Int. 59, 232–243. https://doi.org/10.1016/

j.envint.2013.06.011.
Danzl, E., Sei, K., Soda, S., Ike, M., Fujita, M., 2009. Biodegradation of bisphenol A, bisphenol F and bisphenol S in seawater. Int. J. Environ. Res. Public Health 6, 1472–1484. https://doi.org/10.3390/ijerph6041472.
Deshayes, S., Eudes, V., Bigourie, M., Droguet, C., Moilleron, R., 2017. Alkylphenol and phthalate contamination of all sources of greywater from French households. Sci. Total Environ. 599–600, 883–890. https://doi.org/10.1016/j.scitotenv.2017.05.038.
Domínguez-Morueco, N., González-Alonso, S., Valcárcel, Y., 2014. Phthalate occurrence in rivers and tap water from central Spain. Sci. Total Environ. 500–501, 139–146. https://doi.org/10.1016/j.scitotenv.2014.08.098.
Fauvelle, V., Castro-Jiménez, J., Schmidt, N., Carlez, B., Panagiotopoulos, C., Sempéré, R., 2018. One-single extraction procedure for the simultaneous determination of a wide range of polar and nonpolar organic contaminants in seawater. Front. Mar. Sci. 5, 1–10. https://doi.org/10.3389/fmars.2018.00295.
Fernández-Amado, M., Prieto-Blanco, M.C., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2017. A comparative study of extractant and chromatographic phases for the rapid and sensitive determination of six phthalates in rainwater samples. Chemosphere 175, 52–65. https://doi.org/10.1016/j.chemosphere.2017.02.001.
Fries, E., Püttmann, W., 2003. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in river water and ground water (Oder, Germany). J. Environ. Monit. 5, 346–352. https://doi.org/10.1039/b210342g.
Guigue, C., Tedetti, M., Ferretto, N., Garcia, N., Méjanelle, L., Goutx, M., 2014. Spatial and seasonal variabilities of dissolved hydrocarbons in surface waters from the Northwestern Mediterranean Sea: results from one year intensive sampling. Sci. Total Environ. 466–467, 650–662. https://doi.org/10.1016/j.scitotenv.2013.07.082.
Guo, J., Romanak, K., Westenbroek, S., Hites, R.A., Venier, M., 2017. Current-use flame retardants in the water of lake Michigan tributaries. Environ. Sci. Technol. 51, 9960–9969. https://doi.org/10.1021/acs.est.7b01294.
Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. J. Hazard Mater. 344, 179–199. https://doi.org/10.1016/j.jhazmat.2017.10.014.
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.
Herrero, A., Vila, J., Eljarrat, E., Ginebreda, A., Sabater, S., Batalla, R.J., Barceló, D., 2018. Transport of sediment borne contaminants in a Mediterranean river during a high flow event. Sci. Total Environ. 633, 1392–1402. https://doi.org/10.1016/j.scitotenv.2018.03.205.
Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. 586, 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190.
Ike, M., Chen, M.Y., Danzl, E., Sei, K., Fujita, M., 2006. Biodegradation of a variety of bisphenols under aerobic and anaerobic conditions. Water Sci. Technol. 53, 153–159.
Jin, H., Zhu, L., 2016. Occurrence and partitioning of bisphenol analogues in water and sediment from liaohe river basin and taihu lake, China. Water Res. 103, 343–351. https://doi.org/10.1016/j.watres.2016.07.059.
Kang, J.H., Kondo, F., 2005. Bisphenol A degradation in seawater is different from that in river water. Chemosphere 60, 1288–1292. https://doi.org/10.1016/j.chemosphere.2005.01.058.
Karlsson, T.M., Hassellöv, M., Jakubowicz, I., 2018. Influence of thermooxidative degradation on the in situ fate of polyethylene in temperate coastal waters. Mar. Pollut. Bull. 135, 187–194. https://doi.org/10.1016/j.marpolbul.2018.07.015.
León, V.M., García, I., González, E., Samper, R., Fernández-González, V., Muniategui-Lorenzo, S., 2018. Potential transfer of organic pollutants from littoral plastics debris to the marine environment. Environ. Pollut. 236, 442–453. https://doi.org/10.1016/j.envpol.2018.01.114.
Li, R., Liang, J., Duan, H., Gong, Z., 2017a. Spatial distribution and seasonal variation of phthalate esters in the Jiulong River estuary, Southeast China. Mar. Pollut. Bull. 122, 38–46. https://doi.org/10.1016/j.marpolbul.2017.05.062.
Li, R., Liang, J., Gong, Z., Zhang, N., Duan, H., 2017b. Occurrence, spatial distribution, historical trend and ecological risk of phthalate esters in the Jiulong River, Southeast China. Sci. Total Environ. 580, 388–397. https://doi.org/10.1016/j.scitotenv.2016.11.190.
Liu, Y., Song, N., Guo, R., Xu, H., Zhang, Q., Han, Z., Feng, M., Li, D., Zhang, S., Chen, J., 2018. Occurrence and partitioning behavior of organophosphate esters in surface water and sediment of a shallow Chinese freshwater lake (Taihu Lake): implication for eco-toxicity risk. Chemosphere 202, 255–263. https://doi.org/10.1016/j.chemosphere.2018.03.108.
Loos, R., Tavazzi, S., Mariani, G., Suurkuusk, G., Paracchini, B., Umlauf, G., 2017. Analysis of emerging organic contaminants in water, fish and suspended particulate matter (SPM) in the Joint Danube Survey using solid-phase extraction followed by UHPLC-MS-MS and GC–MS analysis. Sci. Total Environ. 607–608, 1201–1212. https://doi.org/10.1016/j.scitotenv.2017.07.039.
Manikkam, M., Tracey, R., Guerrero-Bosagna, C., Skinner, M.K., 2013. Plastics derived endocrine disruptors (BPA, DEHP and DBP) induce epigenetic transgenerational inheritance of obesity, reproductive disease and sperm epimutations. PLoS One 8. https://doi.org/10.1371/journal.pone.0055387.
Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Scharf, S., Gans, O., 2007. Determination of selected organophosphate esters in the aquatic environment of Austria. Sci. Total Environ. 388, 290–299. https://doi.org/10.1016/j.scitotenv.2007.08.005.
Miège, C., Peretti, A., Labadie, P., Budzinski, H., Le Bizec, B., Vorkamp, K., Tronczynski, J., Persat, H., Coquery, M., Babut, M., 2012. Occurrence of priority and emerging organic compounds in fishes from the Rhone River (France). Anal. Bioanal. Chem. 404, 2721–2735. https://doi.org/10.1007/s00216-012-6187-0.
Mourier, B., Desmet, M., Van Metre, P.C., Mahler, B.J., Perrodin, Y., Roux, G., Bedell, J.P., Lefèvre, I., Babut, M., 2014. Historical records, sources, and spatial trends of PCBs along the RhÔne River (France). Sci. Total Environ. 476–477, 568–576. https://doi.org/10.1016/j.scitotenv.2014.01.026.
Munoz, G., Giraudel, J.L., Botta, F., Lestremau, F., Dévier, M.H., Budzinski, H., Labadie, P., 2015. Spatial distribution and partitioning behavior of selected poly- and perfluoroalkyl substances in freshwater ecosystems: a French nationwide survey. Sci. Total Environ. 517, 48–56. https://doi.org/10.1016/j.scitotenv.2015.02.043.
Net, S., Rabodonirina, S., Sghaier, R. Ben, Dumoulin, D., Chbib, C., Tlili, I., Ouddane, B., 2015a. Distribution of phthalates, pesticides and drug residues in the dissolved, particulate and sedimentary phases from transboundary rivers (France–Belgium). Sci. Total Environ. 521–522, 152–159. https://doi.org/10.1016/j.scitotenv.2015.03.087.
Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B., 2015b. Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. Environ. Sci. Technol. 49, 4019–4035. https://doi.org/10.1021/es505233b.
Noyes, P.D., McElwee, M.K., Miller, H.D., Clark, B.W., Van Tiem, L.A., Walcott, K.C., Erwin, K.N., Levin, E.D., 2009. The toxicology of climate change: environmental contaminants in a warming world. Environ. Int. 35, 971–986. https://doi.org/10.1016/j.envint.2009.02.006.
Olivier, J., Lamouroux, N., Malard, F., Amoros, C., 2009. The Rhône River Basin. https://doi.org/10.1016/B978-0-12-369449-2.00007-2.
Paluselli, A., Aminot, Y., Galgani, F., Net, S., Sempéré, 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.pocean.2017.06.002.
Paluselli, A., Fauvelle, V., Galgani, F., Sempéré, R., 2019. Phthalate release from plastic fragments and degradation in seawater. Environ. Sci. Technol. 53, 166–175. https://doi.org/10.1021/acs.est.8b05083.
Paluselli, A., Fauvelle, V., Schmidt, N., Galgani, F., Net, S., Sempéré, 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.
Panagiotopoulos, C., Sempéré, R., Para, J., Raimbault, P., Rabouille, C., Charrière, B., 2012. The composition and flux of particulate and dissolved carbohydrates from the Rhone River into the Mediterranean Sea. Biogeosciences 9, 1827–1844. https://doi.org/10.5194/bg-9-1827-2012.
Pantelaki, I., Voutsa, D., 2019. Organophosphate flame retardants (OPFRs): a review on analytical methods and occurrence in wastewater and aquatic environment. Sci. Total Environ. 649, 247–263. https://doi.org/10.1016/j.scitotenv.2018.08.286.
Para, J., Coble, P.G., Charrière, B., Tedetti, M., Fontana, C., Sempéré, R., 2010. Fluorescence and absorption properties of chromophoric dissolved organic matter (CDOM) in coastal surface waters of the northwestern Mediterranean Sea, influence of the Rhône River. Biogeosciences 7, 4083–4103.
Peijnenburg, W.J.G.M., Struijs, J., 2006. Occurrence of phthalate esters in the environment of The Netherlands. Ecotoxicol. Environ. Saf. 63, 204–215. https://doi.org/10.1016/j.ecoenv.2005.07.023.
Pivnenko, K., Laner, D., Astrup, T.F., 2018. Dynamics of bisphenol A (BPA) and bisphenol S (BPS) in the European paper cycle: need for concern? Resour. Conserv. Recycl. 133, 278–287. https://doi.org/10.1016/j.resconrec.2018.01.021.
Pont, D., Simonnet, J.P., Walter, A.V., 2002. Medium-term changes in suspended sediment delivery to the ocean: consequences of catchment heterogeneity and river management (Rhône River, France). Estuar. Coast Shelf Sci. 54, 1–18. https://doi.org/10.1006/ecss.2001.0829.
Quinnies, K.M., Harris, E.P., Snyder, R.W., Sumner, S.S., Rissman, E.F., 2017. Direct and transgenerational effects of low doses of perinatal Di-(2-ethylhexyl) phthalate (DEHP) on social behaviors in mice. PLoS One 12, 1–19. https://doi.org/10.1371/journal.pone.0171977.
Raimbault, P., Garcia, N., Cerutti, F., 2008. Distribution of inorganic and organic nutrients in the South Pacific Ocean – evidence for long-term accumulation of organic matter in nitrogen-depleted waters. Biogeosciences 5, 281–298. https://doi.org/10.5194/bg-5-281-2008.
Revathi, P., Saipriya, K., Kumar, C.K., Kumar, T., 2014. Determination of dissolved TBP in PUREX process aqueous streams using ICP-AES. J. Radioanal. Nucl. Chem. 300, 93–98. https://doi.org/10.1007/s10967-014-2994-4.
Sánchez-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.
Schmidt, C., Krauth, T., Wagner, S., 2017. Export of plastic debris by rivers into the sea. Environ. Sci. Technol. 51, 12246–12253. https://doi.org/10.1021/acs.est.7b02368.
Schmidt, N., Fauvelle, V., Ody, A., Castro-Jiménez, J., Jouanno, J., Changeux, T., Thibaut, T., Sempéré, R., 2019. The amazon river: a major source of organic plastic additives to the tropical north atlantic? Environ. Sci. Technol. 53, 7513–7521. https://doi.org/10.1021/acs.est.9b01585.
Schmidt, N., Thibault, D., Galgani, F., Paluselli, A., Sempéré, R., 2018. Occurrence of

microplastics in surface waters of the Gulf of lion (NW Mediterranean Sea). Prog. Oceanogr. 163, 214–220. https://doi.org/10.1016/j.pocean.2017.11.010.
Sempéré, R., Charrière, B., Castro-Jiménez, J., Kawamura, K., Panagiotopoulos, C., 2018. Occurrence of α, ω-dicarboxylic acids and ω-oxoacids in surface waters of the rhone River and fluxes into the Mediterranean Sea. Prog. Oceanogr. 163, 136–146. https://doi.org/10.1016/j.pocean.2017.07.002.
Sempéré, R., Charrière, B., Van Wambeke, F., Cauwet, G., 2000. Carbon inputs of the Rhône River to the Mediterranean Sea: biogeochemical implications. Glob. Biogeochem. Cycles 14, 669–681. https://doi.org/10.1029/1999GB900069.
Sempéré, R., Tedetti, M., Panagiotopoulos, C., Charrière, B., Van Wambeke, F., 2008. Distribution and bacterial availability of dissolved neutral sugars in the South East Pacific. Biogeosciences 5, 1165–1173.
Slomberg, D.L., Ollivier, P., Radakovitch, O., Baran, N., Sani-Kast, N., Bruchet, A., Scheringer, M., Labille, J., 2017. Insights into natural organic matter and pesticide characterisation and distribution in the Rhone River. Environ. Chem. 14, 64–73. https://doi.org/10.1071/EN16038.
Struglia, M.V., Mariotti, A., Filograsso, A., 2004. River discharge into the Mediterranean sea: climatology and aspects of the observed variability. J. Clim. 17, 4740–4751. https://doi.org/10.1175/JCLI-3225.1.
Teil, M.J., Blanchard, M., Chevreuil, M., 2006. Atmospheric fate of phthalate esters in an urban area (Paris-France). Sci. Total Environ. 354, 212–223. https://doi.org/10.1016/j.scitotenv.2004.12.083.
Teil, M.J., Blanchard, M., Dargnat, C., Larcher-Tiphagne, K., Chevreuil, M., 2007. Occurrence of phthalate diesters in rivers of the Paris district (France). Hydrol. Process. 21, 2515–2525. https://doi.org/10.1002/hyp.
Tran, B.C., Teil, M.J., Blanchard, M., Alliot, F., Chevreuil, M., 2015. BPA and phthalate fate in a sewage network and an elementary river of France. Influence of hydroclimatic conditions. Chemosphere 119, 43–51. https://doi.org/10.1016/j.chemosphere.2014.04.036.
Van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B.D., Van Franeker, J.A., Eriksen, M., Siegel, D., Galgani, F., Law, K.L., 2015. A global inventory of small floating plastic debris. Environ. Res. Lett. 10, 124006. https://doi.org/10.1088/1748-9326/10/12/124006.
Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., Wolschke, H., Tian, C., Pan, X., Luo, Y., Ebinghaus, R., 2015. Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China. Environ. Pollut. 198, 172–178. https://doi.org/10.1016/j.envpol.2014.12.037.
Wei, G.L., Li, D.Q., Zhuo, M.N., Liao, Y.S., Xie, Z.Y., Guo, T.L., Li, J.J., Zhang, S.Y., Liang, Z.Q., 2015. Organophosphorus flame retardants and plasticizers: sources, occurrence, toxicity and human exposure. Environ. Pollut. 196, 29–46. https://doi.org/10.1016/j.envpol.2014.09.012.
Wolschke, H., Sühring, R., Xie, Z., Ebinghaus, R., 2015. Organophosphorus flame retardants and plasticizers in the aquatic environment: a case study of the Elbe River, Germany. Environ. Pollut. 206, 488–493. https://doi.org/10.1016/j.envpol.2015.08.002.
Wong, Y.M., Li, R., Lee, C.K.F., Wan, H.T., Wong, C.K.C., 2017. The measurement of bisphenol A and its analogues, perfluorinated compounds in twenty species of freshwater and marine fishes, a time-trend comparison and human health based assessment. Mar. Pollut. Bull. 124, 743–752. https://doi.org/10.1016/j.marpolbul.2017.05.046.
Yamazaki, E., Yamashita, N., Taniyasu, S., Lam, J., Lam, P.K.S., Moon, H.B., Jeong, Y., Kannan, P., Achyuthan, H., Munuswamy, N., Kannan, K., 2015. Bisphenol A and other bisphenol analogues including BPS and BPF in surface water samples from Japan, China, Korea and India. Ecotoxicol. Environ. Saf. 122, 565–572. https://doi.org/10.1016/j.ecoenv.2015.09.029.