Environmental Pollution 309 (2022) 119742

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Assessment of the contamination by 2,4,6-tribromophenol of marine waters and organisms exposed to chlorination discharges☆

Julien Dron [a,*], Carine Demelas [b], Justine Mas [a,b], Amandine Durand [b], Anthony Pantalacci [a], Annabelle Austruy [a], Marine Périot [a], Gautier Revenko [a], Didier Gori [b], Karine Lebaron [b,c], Stéphane Coupé [c], Patrick Höhener [b], Jean-Luc Boudenne [b]

[a] Institut Écocitoyen pour La Connaissance des Pollutions, Fos-sur-Mer, France
[b] Aix Marseille Univ, CNRS, LCE, Marseille, France
[c] Université de Toulon, Aix Marseille Univ, CNRS, IRD, MIO, Marseille, France

ARTICLE INFO

Keywords:
Disinfection by-products
Seawater
Fish
Sea urchin
Mussel
Bioaccumulation

ABSTRACT

2,4,6-tribromophenol (TBP) is implied in the production of brominated flame retardants but is also a major chlorination by-product in seawater. A growing number of studies indicate that TBP is highly toxic to the marine biota, but the contribution of anthropogenic sources among natural production is still under question concerning its bioaccumulation in marine organisms. Here, several water sampling campaigns were carried out in the industrialized Gulf of Fos (northwestern Mediterranean Sea, France) and clearly showed the predominant incidence of industrial chlorination discharges on the TBP levels in water, at the 1–10 ng L^{-1} level in average and reaching up to 580 ng L^{-1} near the outlets. The bioaccumulation of TBP was measured in 90 biota samples from the Gulf of Fos. The concentrations found in European conger muscle tissues (140–1000 ng g^{-1} lipid weight, in average), purple sea urchin gonads (830–880 ng g^{-1} lipid weight, in average), and Mediterranean mussel body (1500–2000 ng g^{-1} lipid weight, in average) were above all published references. Significant correlations with fish length (European conger) and gonad somatic index (purple sea urchin) were also identified. Comparatively, fish, urchins and mussels from other Mediterranean sites analyzed within this study showed a lower bioaccumulation level of TBP, consistently with what found elsewhere. Industrial outflows were thus identified as hotspots for TBP in seawater and marine organisms. The environmental risk assessment indicated a high potential toxicity in the industrial Gulf of Fos, in particular near the outlets, and a limited threat to human but toxicological references are lacking.

1. Introduction

Among other brominated flame retardants (BFRs), 2,4,6-tribromophenol (TBP) is considered as an emerging contaminant (Bidleman et al., 2019; Michalowicz et al., 2022). TBP can be used in pesticides, as a BFR or through the synthesis of other BFRs and is a degradation product of several BFRs. The industrial production tonnage of TBP appears unclear, for instance, ECHA (2016) indicated Europe registered tonnage above 1000 tons yr^{-1} in 2013, but below 10 tons yr^{-1} in 2014, and former worldwide estimations reported 9500 tons yr^{-1} in 2001 Michalowicz et al., 2022. TBP was found in all environmental compartments, ambient and indoor air, soil, sediment, marine and freshwater, as well as in their related biota (Koch and Sures, 2018; Bidleman et al., 2019; Jia et al., 2020; Michalowicz et al., 2022). The incidence of TBP produced by human activities is receiving a growing concern, as an increasing number of studies demonstrated its high toxicity to aquatic and terrestrial organisms, and potentially to humans. In particular, neurological, reproductive, and developmental effects as well as endocrine disruption potential were identified (Deng et al., 2010; ECHA, 2016; Koch and Sures, 2018; Knudsen et al., 2019; Lebaron et al., 2019; Zheng et al., 2022; Zhou et al., 2023).

In the marine environment, TBP is naturally produced by algae (Koch and Sures, 2018; Bidleman et al., 2019), but was also identified as a chlorination by-product (CBP) for years in urban and industrial outlets (Khalanski and Jenner, 2012; Boudjellaba et al., 2016; Zhang et al., 2020). Among urban effluents, industrial chlorination systems are

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.
* Corresponding author.
E-mail address: julien.dron@institut-ecocitoyen.fr (J. Dron).

https://doi.org/10.1016/j.envpol.2022.119742
Received 26 April 2022; Received in revised form 4 July 2022; Accepted 5 July 2022
Available online 11 July 2022

widely employed to prevent biological contamination in desalination plants and ship ballast waters (Agus and Sedlak, 2010; IMO, 2008), and to hinder the biofouling of water pipes or heat exchangers in power plants, gas terminals, and other industries (Khalanski and Jenner, 2012; Quivet et al., 2022). After the quick conversion of $HOCl/OCl^-$ to $HOBr/OBr^-$ in seawater containing high levels of bromide, further reactions with organic matter produce various brominated CBPs among which bromophenols such as TBP (Heeb et al., 2014).

Nevertheless, the reporting of TBP measurements in marine waters, sediments and biota in exposed environments is still scarce in the literature. A few works reported TBP seawater levels, around 1.5 μg L^{-1} (Boudjellaba et al., 2016) and 1.5–2.1 ng g^{-1} in sediment (Manasfi et al., 2019) in the vicinity of industrial chlorination outlets, and still measured several km away from the source point (Korean nuclear power plant) at levels up to 0.020 μg L^{-1} in water and 12 ng g^{-1} in sediment (Sim et al., 2009). Among marine species, TBP was principally measured in fish with average levels from 12 ng g^{-1} lipid weight (lw) in a remote area (Schlabach et al., 2011) to 1900 ng g^{-1} lw in the industrialized Gulf of Fos (Boudjellaba et al., 2016) and mussel from 21 ng g^{-1} lw away from sources (Löfstrand et al., 2010) to 630 ng g^{-1} lw in an urban environment (Schlabach et al., 2011). However, assessing the contribution of anthropogenic sources to the TBP levels measured in the marine environment and biota remains generally uncertain (Bidleman et al., 2019). On the other hand, an increasing number of studies reveals the acute and chronic toxicity of TBP to marine organisms, acting as an endocrine disruptor, affecting reproduction and larval growth among other (Schäfer et al., 2009; Li et al., 2009; Folle et al., 2020; Fu et al., 2020; Zhou et al., 2023). It has been also shown that cocktail effects may occur with accompanying CBPs (Lebaron et al., 2019), and that TBP may also be a precursor to other relevant contaminants (Arnoldsson et al., 2012).

Today, chlorination remains the main industrial treatment process of seawater to limit biofilm growth or mollusk settlements in pipes and in heat exchangers, used in various industrial uses such as desalination, petrochemical, steel, nuclear and thermal facilities (Boudjellaba et al., 2016; Grote et al., 2022), and could even expand in the future due to the guidelines in ship ballast water management favoring chlorination (IMO, 2008). Therefore, a better evaluation of the potential contamination of marine ecosystems by TBP anthropogenic sources appears essential. To our knowledge, the previous works investigating TBP in the marine environment were generally limited to one-shot measurements in water (Sim et al., 2009; Khalanski and Jenner, 2012; Boudjellaba et al., 2016; Manasfi et al., 2019), a single marine specie analysis (Wu et al., 2019) or single geographical location (Dahlgren et al., 2016). It was also often a secondary result with limited interpretations and discussion among other contaminants studies (Dahlberg et al., 2016a, 2016b; Bidleman et al., 2019).

In the present study, we aimed at evaluating TBP concentrations in marine waters, as well as determining TBP in marine species of contrasted biological characteristics and potential exposure routes, in order to better assess the incidence of chlorination outlets on TBP spread in the marine ecosystem on the basis of statistically relevant data. Water was thus collected from the outlets to several km away during 7 campaigns covering all seasons and various meteorological conditions, also completed by the few previous punctual data (Boudjellaba et al., 2016; Manasfi et al., 2019). We also first report the determination of TBP by both spot and passive sampling together in an exposed area. TBP was also determined in three marine organisms of different trophic level and living habitat (*Conger conger*, *Paracentrotus lividus* and *Mytilus galloprovinciallis*), originating from the Gulf of Fos hosting several chlorination discharges, as well as from unexposed locations in the French Mediterranean. The sampling design of biota, including a high number of samples of the three species in the exposed area, enabled to focus on the parameters driving the bioaccumulation of TBP in these marine organisms. These results, combined to a comparison with the concentrations recorded in unexposed places for the same species, permitted to further discuss the potential risks to marine life and human health.

2. Materials and methods

2.1. Study area

The Gulf of Fos is a highly industrialized semi-enclosed bay located in the northwestern Mediterranean coast, subjected to freshwater inputs from the Rhône River and the Berre Lagoon. It hosts the greatest French harbor, where two liquefied natural gas (LNG) terminals, two power plants, petrochemical facilities and a steel production complex, employ chlorination techniques (hypochlorite injection or seawater electrochlorination) to maintain water pipes and heat exchangers effective (Boudjellaba et al., 2016). Typical chlorine operating targets are 1 mg Cl_2 L^{-1} and are requested to be kept below 0.1 mg Cl_2 L^{-1} in the outlets. During the studied period, the average cumulative flow of the chlorination discharges (of which data was available), was 39 144 m^3 h^{-1}, with monthly averages varying between 15 000 and 70 000 m^3 h^{-1}. It should be noted that we were unable to obtain any flow data for two major outlets (steel industry and petrochemical complex), but our observations during the field campaigns indicated that they were permanently active with estimated flows of approximately 20 000 m^3 h^{-1} each. Previous observations also showed that chlorinated waters were released in these outlets (Boudjellaba et al., 2016; Manasfi et al., 2019). Compared to seawater, the water temperature in the outlets showed differences down to $\Delta T = -6$ °C in the LNG regasification releases, and up to $\Delta T = +8$ °C in the power plants discharges, and +5 °C in the steel and petrochemical complex outflows. A seasonal variability was noticed, with reduced outlet flows during summer due to the lower activity of power plants (Supporting Information S1).

2.2. Water sampling and analysis

The collection of water samples was realized in 26 sites, covering the known chlorination discharges (N = 7), the Rhône River and the Gulf of Fos. Sampling was carried out at the surface and 7 m deep (or 1 m above the bottom in shallower waters), for each of the 7 boat campaigns (April 2017, October 2017, February 2018, June 2018, November 2018, June 2019, June 2020, Supporting Information S1). A 5 L Niskin PVC bottle was employed to collect water. Bottle blank runs showed no detectable levels of TBP. As fully described by Manasfi et al. (2019), the seawater samples were transferred to 1 L amber glass bottles and ascorbic acid was immediately added. Back to laboratory, within a few hours from sampling, 0.5 g sodium carbonate and 0.5 mL acetic anhydride were added to 50 mL samples to derivatize TBP by acetylation. Samples were then extracted with MTBE and spiked with the internal standard 2,4,6-trichlorophenol (TCP). The organic phase was analyzed by GC/ECD (Clarus 580, PerkinElmer, USA). Calibration was carried out in standard solution and also by mean of the standard addition method. The identification of TBP was regularly verified by GC/MS runs. The detection limit was 3 ng L^{-1} of seawater, and the analytical relative standard deviation (RSD) was 1.6% in the range of quantification (10–1000 ng L^{-1}). Blank runs were realized between each sample and calibration was verified before, in the middle and after each analysis sequence.

2.3. Qualitative determination of TBP in passive samplers

Two Chemcatcher® (T.E Laboratories Ltd, Ireland) configurations were tested in PTFE holders, the Empore™ C18 receiving disk associated to a low-density polyethylene (LDPE) diffusive membrane, and the Atlantic™ HLB-L receiving disk to a polyethersulphone (PES) diffusive membrane. The PTFE holders were soaked in acetone for 12 h and rinsed with ultrapure water after ultrasonic cleaning. The C18 and HLB receiving phase, and the PES membrane were prepared by soaking for 12 h in methanol, and the LDPE membrane in n-hexane, according to recommendations (Vrana et al., 2007). All were rinsed and stored with

ultrapure water. The field deployment of the Chemcatcher® was carried out for 28 and 35 days, around the spot sampling campaigns realized in June 2019 and June 2020, respectively. The devices were screwed on stainless steel disks, and hanged from navigation buoys, at approximately 2 m depth.

After exposure, an internal standard was added (2,4,6-TCP) and the receiving phases were rinsed with ultrapure water and extracted in an ultrasonic bath with 15 mL dichloromethane for 10 min and again with 21 mL of a hexane/acetone mixture (75/25 v/v) for 10 min. The organic phases were dried with sodium sulfate and filtered through 0.22 µm PTFE filters. The analysis was then carried out by GC-MS/MS (Trace GC Ultra coupled to a TSQ Quantum™ Triple Quadrupole, Thermo Scientific). The GC conditions temperature program were the same as for water analysis (Manasfi et al., 2019) and TBP was determined by electronic impact ionization and multiple reaction monitoring (MRM, collision energy 20 eV) with m/z 221.7 and m/z 141.2 as precursor and product ions, respectively. Full MS mass spectra were also regularly recorded to ensure the identification of TBP. Calibration was carried out similarly to water spot samples analysis, using 2,4,5-TCP as internal standard, and repeated before and after each analysis sequence. Analytical RSD was 1.9% and limit of detection 0.3 µg L^{-1} in the extract. The extraction efficiency was measured after stirring for 7 days the devices in a synthetic seawater bath spiked with TBP at 200 µg L^{-1}, with very satisfying yields for both HLB-L (100.9%) and C18 (79.4%) configurations. Blank tests showed that the prepared Chemcatcher® devices did not release detectable traces of TBP.

As the aim of this preliminary experiment was first qualitative, an approximate sampling rate (R_S) value was deduced from the empirical model developed by Vrana et al. (2007) for the C18 configuration, considering log K_{OW}(TBP) = 4.13 (NCBI, 2021). It resulted in R_S = 0.182 L d^{-1}, falling in the range of other phenolic compounds, 2, 4-dichlorophenol (Nyoni et al., 2010) alkylphenols and bisphenol-A (Chen et al., 2020). Studies using the HLB/PES configuration report R_S values in the range 0.010–0.100 L d^{-1} for bisphenol-A and pesticides (Petrie et al., 2016; Grodtke et al., 2021), also an intermediate value R_S = 0.050 L d^{-1} was arbitrary applied here.

2.4. Samples from marine organisms

The marine organisms were collected throughout the Gulf of Fos, and for comparison purposes, away from industrial chlorination effluents (Fig. 1), in the Port-Cros National Park (PC-NP, 100 km east), in the Sète region (80 km west) and in Corsica (STARESO scientific station). A summary of the main physiological parameters of marine biota is provided in Supporting Information S2, and full data in a separate CSV file (Supplementary data). The European conger (*Conger Conger*) is a benthic and sedentary fish, at the top of the trophic level in the Gulf of Fos. Its characteristics make it a reliable bioindicator for marine pollutants monitoring, including TBP, at fine spatial scales (Dron et al., 2019). The specimens were captured by means of bottom long-lines, measured and weighted, and immediately brought to the laboratory to remove muscle tissues which were stored at −40 °C. Purple sea urchin (*Paracentrotus lividus*) is a well-known model for marine ecotoxicological studies, recently employed to assess the toxicity of chlorination by-products including TBP (Lebaron et al., 2019). They were collected within 50 m from shore, measured and weighted. The Mediterranean mussel (*Mytilus galloprovincialis*) is a filter feeder extensively used for marine biomonitoring purposes (Andral et al., 2011). Mussels were collected on 5 navigation buoys throughout the Gulf of Fos, and within 50 from shore in the other locations, except in Sète (Thau Lagoon), where they were obtained from a local producer just after harvesting. They were immediately placed in 10 L of seawater sampled locally for 24 h at room temperature (21 °C), measured and weighted. In each site, at least 40 urchins and mussels of the largest dimensions were chosen and split into 2 to 4 sub-samples, equivalent in organism size distributions and number (10–20 depending on sites). After test or shell and byssus removal, urchin gonads and mussel soft tissues were weighted again and stored at −40 °C.

All biota samples were freeze-dried, ground to fine powder with a ball mill equipped with ZrO_2 beads and capsules, and kept at −40 °C. The lipid content was determined following the Folch method (Pérez-Palacios et al., 2008). The C and N elemental composition and the stable isotope ratios $\delta^{13}C$ and $\delta^{15}N$ were calculated by determining in 400 µg aliquots packaged in tin microcapsules, with a continuous flow isotope ratio mass spectrometer coupled to an organic elemental analyzer (Thermo Scientific, DELTA V and Flash HT plus).

2.5. Extraction and analysis of TBP in marine organisms

All solvents were of analytical grade and standard stock solutions of TCP and TBP were prepared in dried acetonitrile. TBP was determined from 2 g of tissues spiked with 25 µL TCP solution (10 mg L^{-1}). The

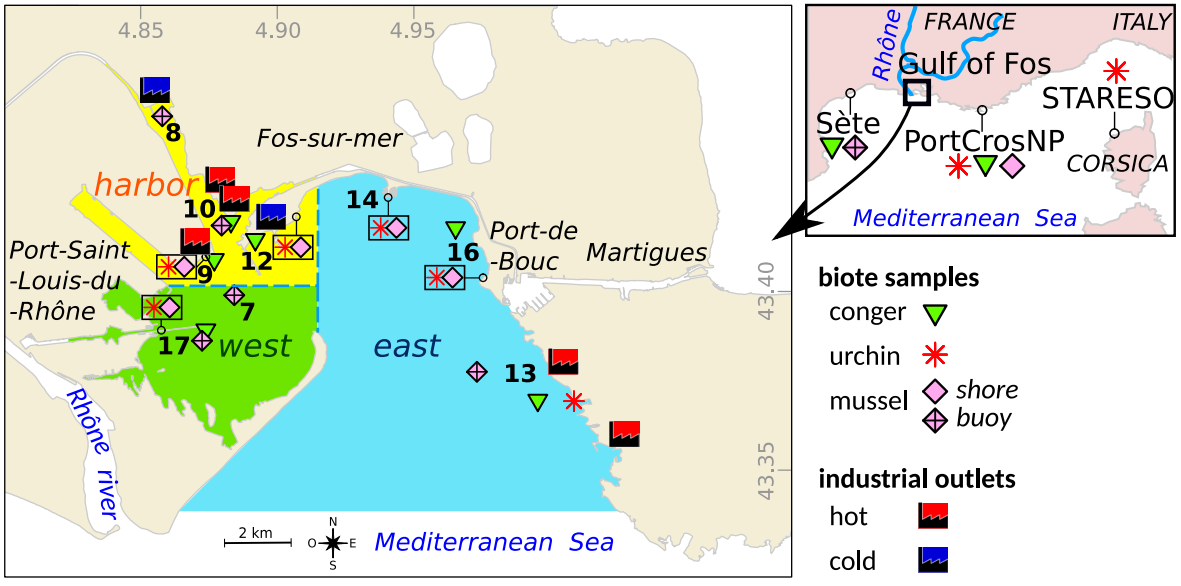


Fig. 1. Locations identified by numbers of marine biota harvesting sites of European conger, purple sea urchins, and Mediterranean mussel. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

extraction method, inspired from Hong et al. (2004) and Ahn et al. (2007), was carried out by 30 min sonication in 50 mL dichloromethane/acetone (50:50, v/v). The extract was filtered (PTFE 0.45 μm) and evaporated under a gentle stream of nitrogen. 5 mL of n-hexane were added and loaded on a Florisil SPE cartridge (1 g/6 mL, Restek, USA, conditioned with 6 mL n-hexane) for further clean-up. The elution was realized with 2 × 3 mL n-hexane/acetone (75:25, v/v). The solution was evaporated to 0.5 mL and finally diluted to 5 mL in n-hexane. The extraction recovery, calculated from spiked samples, was 101.7% (N = 5).

The sample extracts were analyzed by GC/ECD, equipped with a 30 m × 0.25 mm × 1 μm column (Elite-5MS, PerkinElmer). Helium 5.0 was used as the carrier gas at a flow rate of 1 mL min^{-1}, and nitrogen as make-up gas (30 mL min^{-1}). The injector temperature was 200 °C and the program started at 65 °C held for 5 min, increased at 2 °C min^{-1} to 240 °C, finally increased at 40 °C min^{-1} to 310 °C, held for 10 min. The calibration was defined using 8 concentration levels within a linearity range of 1–100 μg L^{-1}, resulting in $R^2 > 0.99$ and 0.97 in standard solution and spiked biota extract, respectively. The repeatability of the analytical method (N = 10) was 11% and 17%, respectively. The identification of TBP was regularly ensured through GC/MS runs. The detection and quantification limits (3 and 10 times the blank standard deviation, respectively, N = 10) determined at low concentration level were 0.27 ng g^{-1} dry weight (dw) and 0.95 ng g^{-1} dw of biota tissue, respectively. Blank runs were realized between each sample and calibration was verified by analyzing the whole set of calibration levels, before, in the middle and at the end of each analysis sequence.

2.6. Data analyses

All the statistical analyses and graphics were realized with the R software (R Core Team, 2020) and Inkscape (www.inkscape.org).

As in previous works (Dron et al., 2019), the Gulf of Fos was divided into three areas (harbor, east and west), on the basis of isotope ratios $\delta^{13}C$ and $\delta^{15}N$ adjusted to fish length in European conger muscle tissues (Fig. 1). The geographical discrimination was very comparable to what obtained in European conger fished 5 years earlier (Dron et al., 2019), corroborating the specificity of the 3 areas, in particular among freshwater inputs (Supporting Information S3).

The influence of biological parameters on TBP concentrations in marine organisms was evaluated through multilinear regressions. They were restricted to the Gulf of Fos to avoid geographical influences as expected from the very different isotope ratios observed in the other locations studied (Supporting Information S2). Stepwise multilinear regression was applied using the backward elimination of the parameter with the lowest Student t-value to minimize the global p-value, and a new analysis carried out until 3 variables remained. Then, cross-product terms were included. The best models were qualified considering global and individual p-values, after verification that the residuals fulfilled the Shapiro-Wilk normality test.

Due to the limited number of samples in reference zones, Mann-Whitney rank tests (non-parametric Wilcoxon median comparison tests) were realized to evaluate significant differences between locations ($p < 0.05$).

3. Results and discussion

3.1. TBP in industrial outlets and marine waters

Quantifiable levels of TBP were found for each campaign except in October 2017 (Supporting Information S4), in at least one of the industrial outlets and two harbor sites nearby (8p and 7p, Fig. 2). TBP was detected once in the harbor entrance (site 7p, 41 ng L^{-1}), in the steel complex outlet (site 10x, always active, *i.e.* visible outflow) and in the power plants releases in site 9x (active in 5 out of 7 campaigns) and in site 11x (active in 6 campaigns). On the other hand, in the LNG outlets, it was found twice in both sites 8x and 8p (active in 3 campaigns), and three times in site 12x (active in 6 campaigns). The TBP levels reached up to 580, 220 and 430 ng L^{-1} in sites 8x, 8p and 12x, respectively, but only 48, 88 and 140 ng L^{-1} in the warmed waters of sites 11x, 9x and 10x, respectively. The higher concentrations in the LNG outlets suggested that the cooled chlorinated waters produced through the regasification process could favor the formation of TBP. Unlike Boudjellaba et al. (2016) which reported higher TBP levels during winter but no detectable concentrations during summer, no seasonality was observed here. Comparable levels were found in the chlorinated waters outflows of nuclear power plants (Allonier et al., 1999; Sim et al., 2009) and ship ballast (Delacroix et al., 2013). Away from discharge outlets, the

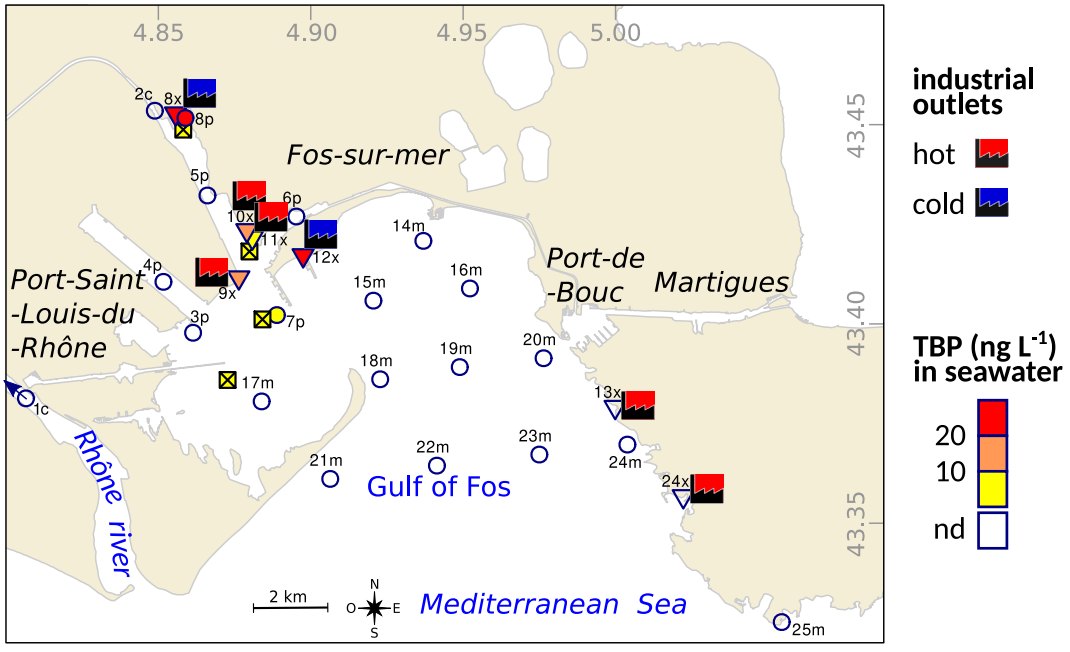


Fig. 2. Locations identified by numbers of water spot sampling (triangles = industrial outlets, circles = other) and passive sampling (cross boxes) colored among TBP mean concentrations.

concentrations found in the literature dropped below 5 ng L^{-1} (Reineke et al., 2006; Sim et al., 2009) or even below 0.3 ng L^{-1} in remote sites (Vetter et al., 2018), more than one order of magnitude below the concentrations measured punctually in sites 8p and 7p.

As reported in previous works (Boudjellaba et al., 2016; Manasfi et al., 2019), TBP was never detected in the Rhône River (site 1c), thus not representing a significant input to the Gulf of Fos. TBP was neither detected in the sites located offshore (Fig. 2). Consequently, it clearly appeared that the local industrial chlorination discharges were the very predominant source of TBP in the Gulf of Fos, further diluting or degrading below detection limits.

To our knowledge, passive samplers were employed here for the first time in an exposed area to determine TBP in water, and similarly to a previous study in remote ocean (Vetter et al., 2018), the aim of this primary approach was to evaluate the capabilities of the Chemcatcher® device and limited to qualitative measurements. The Chemcatcher® devices were located in the vicinity (150–300 m distance) of industrial outlets, by sites 8p, 10x, and 12x, as well as in the more distant site 17 m (Fig. 2). TBP was detected in all samples extracted from HLB-L membranes, with higher levels found in June 2019 than in June 2020 (1.0–1.5 and 0.2–0.7 ng L^{-1}, respectively, and considering $R_S = 0.050$ L d^{-1}). It was also detected in all samples extracted from C18 membranes in June 2019 (0.2–0.4 ng L^{-1}, considering $R_S = 0.182$ L d^{-1}), but not in June 2020 (Supporting Information S5). These levels were homogeneous among the deployment sites, corroborating that TBP may diffuse at levels that were not detectable by spot sampling, supporting further development of this technique.

3.2. TBP levels in the marine biota from the Gulf of Fos and relations with biological parameters

TBP was detected in all the marine organisms sampled in the Gulf of Fos industrial bay (full data is provided in Supplementary data), and the mean concentration levels (Table 1) referred to wet weight (ww) were higher in purple sea urchin gonads (28 ± 10 ng g^{-1} ww), than in Mediterranean mussel soft tissues (16 ± 9 ng g^{-1} ww) and European conger muscles (6.2 ± 3.9 ng g^{-1} ww). Their mean variability calculated between sub-samples (each containing 10–20 pooled individuals) were 22.6% and 31.8% for sea urchin gonads and mussels, indicating a satisfying reproducibility of the whole methodology including sampling, sample preparation, extraction steps, and chemical analysis. The RSDs between conger specimens from single sites were slightly higher (36.3% in average) but were determined at the individual level.

As expected from the log K_{ow} (TBP) and previous works (Löfstrand, 2011; Bidleman et al., 2019), the concentration of TBP in tissues of marine biota was globally well correlated with lipid content ($R^2 = 0.41$,

Table 1
TBP concentration ranges (mean) relative to wet (ww) and lipid weight (lw) in marine biota.

Specie	Sampling location and date	TBP (ng g^{-1} ww)	TBP (ng g^{-1} lw)	Ref.
FISH (muscle)				
Pelagic carnivores	East Australia (1994–95)	nd-0.9 (0.3)		Whitfield et al. (1998)
Benthic carnivores	East Australia (1994–95)	nd-12 (1.5)		Whitfield et al. (1998)
Omnivores	East Australia (1994–95)	nd-4.3 (1.0)		Whitfield et al. (1998)
S. canaliculatus	Hong-Kong (2000)	1.4–11 (5.8)		Chung et al. (2003)
E. areolatus	Hong-Kong (2000)	0.6–6.4 (3.3)		Chung et al. (2003)
G. aculeatus [a,b]	East Sweden (2013)	nd-27 (6.9)	nd-1200 (290) [c]	Dahlgren et al. (2016)
P. fluviatilis [a,b]	East Sweden (2013)	0.3–2.0 (1.3)	6.3–69 (38) [c]	Dahlgren et al. (2016)
S. alpinus [b]	Faroe Islands (remote, 2009)	(0.1)	(12)	Schlabach et al. (2011)
P. fluviatilis [b]	Finland (urban, 2009)	0.1–3.5 (1.1)	8.2–250 (90)	Schlabach et al. (2011)
C. harengus [a]	East Sweden (2013)	0.2–0.9	3.9–12	Dahlberg et al. (2016b)
C. conger	FR Med. (industrial, Fos 2012)	nd-10 (4.6)	nd-8100 (1900)	Boudjellaba et al. (2016)
C. conger	FR Med. (industrial, Fos 2017)	2.0–16 (7.4)	290-2500 (1000)	This study
C. conger	FR Med. (industrial, Fos 2019)	0.9–2.9 (1.6)	54-250 (140)	This study
C. conger	FR Med. (Sète 2019)	1.0–1.2 (1.1)	65-95 (82)	This study
C. conger	FR Med. (PC-NP, 2020)	2.0–4.4 (3.2)	260-610 (460)	This study
BIVALVES (soft tissues)				
Oyster O. rivularis	Hong-Kong (2000)	0.2–1.9 (1.0)		Chung et al. (2003)
Clam *T. philippinarum*	Hong-Kong (2000)	1.1–23 (9.5)		Chung et al. (2003)
M. edulis	South Sweden (2003–06)	0.1–0.4 (0.3)	7.5–35 (21) [c]	Löfstrand et al. (2010)
M. edulis	Norway (urban, 2009)	11-13 (12)	500-770 (630)	Schlabach et al. (2011)
M. edulis	Iceland (remote, 2009)	(3.2)	(460)	Schlabach et al. (2011)
M. edulis	Southeast Sweden (2011–12)	0.4–2.6 (1.0)	17-240 (63)	Dahlberg et al. (2016a)
M. galloprovinciallis	FR Med. buoys (industrial, Fos 2017)	11-26 (16)	800-2500 (1500)	This study
M. galloprovinciallis	FR Med. shore (industrial, Fos 2017)	6.3–47 (19)	410-7100 (2000)	This study
M. galloprovinciallis	FR Med. lagoon (farm, Sète 2020)	6.6–9.9 (8.0)	420-770 (610)	This study
M. galloprovinciallis	FR Med. shore (PC-NP, 2020)	1.5–3.3 (2.1)	220-510 (340)	This study
SEA URCHIN (gonads)				
P. lividus	FR Med. (industrial, Fos 2017)	9.0–54 (27)	240-200 (830)	This study
P. lividus	FR Med. (industrial, Fos 2019)	27-41 (35)	790-960 (880)	This study
P. lividus	Corsica (remote, STARESO 2019)		(490)	This study
P. lividus	FR Med. (PC-NP, 2019)		130-360 (240)	This study
OTHER				
Squid L. reynaudii	South Africa (2017)		1.7–47 (20)	Wu (2019)
Prawns (tails)	East Australia wild (1993–96)	nd-130 (8.8)		Whifield (1997)
Prawns (tails)	East Australia farm (1993–96)	nd-0.2 (0.1)		Whifield (1997)
Gammarus sp.	East Sweden (2013)	9.4–15 (11)	1100-1500 (1300) [c]	Dahlgren et al. (2016)
Alga C. tenuicorne	East Sweden (2013)	0.2–1.2 (0.6)	420-1400 (720) [c]	Dahlgren et al. (2016)
Alga D. foenicolaceus	South Sweden (2003–06)	(0.5)	(180) [c]	Löfstrand et al. (2010)
Bacteria N. spumigena	South Sweden (2003–06)	(0.0004)	(0.2) [c]	Löfstrand et al. (2010)

FR Med.: French Mediterranean.
[a] Whole fish.
[b] Anadromous fish or potentially mixed fresh/marine influence.
[c] Expressed as ng g^{-1} EOM (extractable organic matter).

$p < 0.001$, Fig. 3a). Consequently, the TBP levels in the different marine organisms sampled in the Gulf of Fos were tightened when expressed relative to lipid weight, *i.e.* 840 ng g^{-1} lw in sea urchin gonads, 1800 ng g^{-1} lw in mussel soft tissues, and 820 ng g^{-1} lw in conger muscle (Table 1). Thus, further comparisons and interpretations will be discussed on a lipid weight (lw) basis, except when otherwise indicated. These levels were globally much higher to those reported by other studies in fish and mussel from the Baltic Sea (Table 1) where the highest levels were found in the vicinity of an urban area (Schlabach et al., 2011). Even fewer data were available from other seas but those were also below what measured here in the Gulf of Fos (Chung et al., 2003; Wu et al., 2019). The results obtained in the industrialized Gulf of Fos corroborated the higher levels found by urbanized areas, and more globally that anthropic pressures result in a higher exposure of the marine environment to TBP.

A multilinear regression restricted to European conger and including available biological data (fish length, weight, $\delta^{13}C$ and $\delta^{15}N$, water content), revealed that the TBP concentrations relative to lipid weight were negatively correlated to fish length ($R^2 = 0.50$, $p < 0.001$, Fig. 3b). As fish length can be assimilated to age (Dron et al., 2019), this implied that younger fish accumulated more TBP than older ones. As no significant correlation was found with stable isotopes $\delta^{15}N$ and $\delta^{13}C$ values ($p > 0.1$), biomagnification did not seem to occur through the food chain, at least for European conger. This is corroborated by the similar or lower TBP levels measured in European conger compared to purple sea urchin and Mediterranean mussel, respectively, leading to biomagnification factors, BMF <1 ($BMF = c_{predator}/c_{prey}$), assuming that sea urchin and mussel are potential preys (Lu et al., 2018). European conger feeds

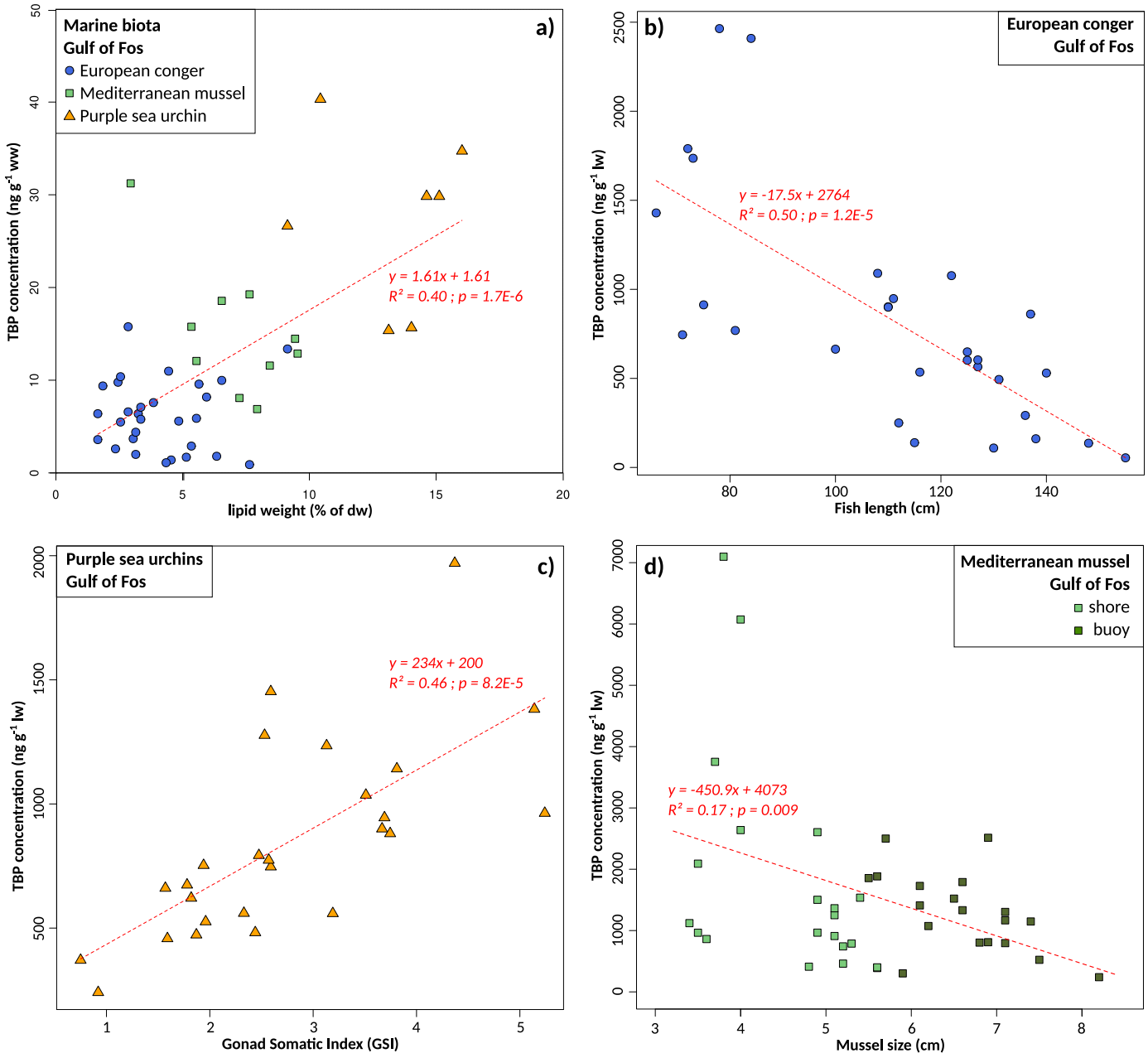


Fig. 3. Correlations between a) all species TBP levels (ng g^{-1} ww) and lipid weight (% of dw), b) European conger TBP levels (ng g^{-1} lw) and fish length (cm), c) purple sea urchins TBP levels (ng g^{-1} lw) and gonad somatic index (GSI), and d) Mediterranean mussel TBP levels (ng g^{-1} lw) and shell size (cm). Urchin and mussel concentrations in a) are pooled, in c) and d) include all sub-samples concentrations. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

principally of small fish, but also cephalopods, crustacean and mollusca (Cau and Manconi, 1984). In European conger from the Gulf of Fos, it was observed that $\delta^{15}N$ values stabilized when total length exceeds 100 cm, and this was attributed to a shift towards settled feeding habits with preys of higher trophic level, or to a physiological change related to a transition from pre-vitellogenic to early vitellogenic stage (Dron et al., 2019). From these observations, the higher accumulation levels of TBP in younger fish suggested the influence of a metabolic change with age, or a biodilution effect due to lower TBP levels in higher trophic level preys. Assuming the preferential accumulation of TBP in fat tissues, it should be also considered that a majority of congers fished were older than three major chlorination installations operating since 2010 only (LNG terminal in 12x and power plants in 9x and 11x). In 2017, 61% were born before 2010 (up to 12 yr old) and 67% in 2019 (up to 15 yr old) (Supplementary data). Further monitoring of European conger should provide some answers and determining TBP in a larger number of species of the local food web should precise the incidence of biodilution.

Similarly to European conger, the TBP concentrations relative to lipid weight in Mediterranean mussel showed a negative correlation with the size of the shell, even though less significant (Fig. 3d). Mediterranean mussel collected from buoys and shore sites had comparable concentration levels, except from site 20 (East shore), where mussel shell size was below 4 cm while it was above 5 cm in most other sites. As reported for PCBs and organochlorine pesticides (Milun et al., 2020), the accumulation of contaminants decreases in larger in mussel. This was very probably due to the changing metabolism and physiology which is associated to a slower growth rate in larger organisms, generally occurring from a 4–6 cm size for this species (Andrisoa et al., 2019). The slower growth rate is associated to a reduced metabolism, resulting in slower accumulation rates for larger individuals, which may also possibly possess higher elimination capacities, both leading to decreasing TBP levels with shell size.

On the other hand, the TBP concentrations were not correlated with the test diameter in purple sea urchins, but positively correlated with the gonad somatic index (GSI) at a significant level ($R^2 = 0.46$, $p < 0.001$, Fig. 3c). This was consistent with the lipophilic character of TBP, as higher GSI and lipid contents are generally associated (Rocha et al., 2019). Similarly, higher nonylphenol levels were measured in spring, also corresponding to higher GSI values, in purple sea urchin from South-East Mediterranean (Amri et al., 2017).

3.3. Impact of chlorination discharges on TBP bioaccumulation

Within the Gulf of Fos, TBP mean levels (ng g^{-1} lw) showed some significant differences among the defined areas (harbor, west, east) in the investigated species (Fig. 4). However, regarding the relations between TBP levels and physiological parameters, it was interesting to compare the results adjusted to fish length, mussel size and sea urchin GSI, according to the regression equations obtained previously (Fig. 3). Thus, the residuals issued from the linear models applied to TBP concentrations toward these parameters showed no significant geographical difference across the Gulf of Fos for European conger and Mediterranean mussel. Only sea urchins from the west and most enclosed part had significantly higher concentrations (Supporting Information S6).

On the other hand, the marine organisms sampled from other locations, supposed away from major chlorination discharges in the NW Mediterranean (Fig. 1), systematically had concentration levels below those found in the Gulf of Fos (Fig. 4). Despite the smaller number of samples, the dispersion of the concentrations in these remote areas were also much lower than in the Gulf of Fos. A high heterogeneity is often characteristic of industrial or at least anthropogenic influence and supports here the hypothesis of the impact of industrial chlorination discharges. Finally, adjusting the TBP levels from remote areas based on the regression equations obtained in the Gulf of Fos (Fig. 3) resulted in median residuals for conger and mussel below those of the Gulf of Fos (Supporting Information S6). The GSI values were not available in

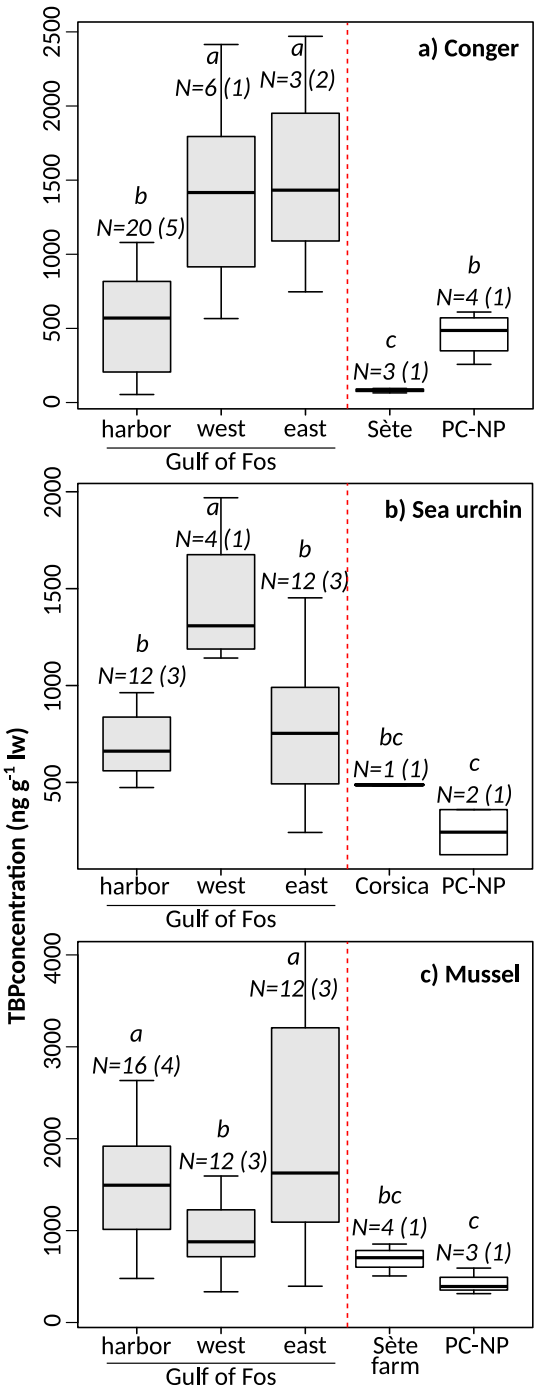


Fig. 4. TBP concentration levels (medians, quartiles and 1.5*interquartile ranges) in the defined zones of the Gulf of Fos (grey), and more remote locations along the French Mediterranean (white) for A) European conger, B) sea urchin, and C) mussel. N is the total number of samples and between brackets the number of harvesting locations. Different letters above boxes indicate significant differences.

reference sites for sea urchins, and their TBP levels could not be adjusted. Even though the linear models from the Gulf of Fos may not be appropriate in other locations, due to the variability in growth and development rates, at least for mussels (Steffani and Branch, 2003), these calculations are in line with the hypothesis that the vicinity of industrial chlorination discharges induce a greater accumulation of TBP in marine organisms.

To the best of our knowledge, the TBP levels recorded in marine biota collected in the Gulf of Fos were superior to what has been previously

reported in the literature, on the contrary to the remote sites studied here (Sète, Corsica, Port-Cros NP) which were globally in the range of most values encountered in other seas (Table 1). Other relatively high levels were reported in blue mussel (*M. edulis*) from an urban area of Norway (Schlabach et al., 2011), as in fish and bivalves from Hong-Kong (Chung et al., 2003), highlighting the potential incidence of urban associated outflows.

Even though international literature remains scarce for TBP in marine biota, the results obtained here indicated a significant influence of chlorination industrial discharges on TBP bioaccumulation in marine species. Further research and data are needed to improve comparisons and interpretations, in contaminated areas, as the data collected here are still insufficient to study TBP pathways from water to bioaccumulation in biota, for instance.

3.4. Environmental risk assessment

As the TBP levels in biota were homogeneous across the Gulf of Fos, the risk assessment was evaluated from the average (0.83 ng L^{-1} considering not-detected = LD/2) and maximum (580 ng L^{-1}) water concentrations over all sampling sites and campaigns (excluding Rhône River and control). A Predicted No-Effect Concentration (PNEC) was calculated using the endpoint values listed in Table 2. According to the ECHA guidance (ECHA, 2008), an assessment factor AF = 10 was applied to the lowest endpoint, resulting in PNEC = 30 ng L^{-1}. This was in accordance with the latest ECHA (2016) estimation (25 ng L^{-1}) and confirms that previous calculations around 500 ng L^{-1} were overestimated due to lacking toxicological references (Schlabach et al., 2011; Delacroix et al., 2013). The corresponding ratios with the Predicted Environmental Concentration (PEC) and Maximal Concentration (PEC_{max}) in the Gulf of Fos were PEC/PNEC = 0.03 and PEC_{max}/PNEC = 19. Beside a high contrast, directly proportional to the difference between average and maximal water concentrations, it suggested that the organisms living in the Gulf of Fos undergo a significant toxicological risk that may be a threat in the long-term, in particular around industrial chlorinated water source points. Concentrations above PNEC occurred in marine water samples for each of the 7 campaigns except in October 2017. Several studies pointed out that TBP may be toxic at low levels (Table 2), supporting that efforts in TBP monitoring should be achieved to improve ecotoxicological evaluations.

Considering averaged wet weight concentrations in biota (ww) sampled from Gulf of Fos and the mean TBP level in seawater, the calculation of field bioaccumulation factors (BAF) resulted in elevated values, from 11 000 L kg^{-1} in European conger muscle, to 28 000 L kg^{-1} in Mediterranean mussel, and 51 000 L kg^{-1} in purple sea urchins. They are much higher than values calculated in a previous study carried out in the Gulf of Fos (BAF = 25 L kg^{-1}), due to that this earlier study mainly focused on exposed sites with TBP water concentrations 100–1000 times higher (Boudjellaba et al., 2016), as observed here. The TBP field BAF values calculated were also much higher than bioconcentration factors (BCF) resulting from laboratory studies and model results (BCF = 20 to 600) (ECHA, 2016; Khalanski and Jenner, 2012). On the other hand, estimations based on Arnot and Gobas (2006) equations were closer, with BAF = 2000–4700 L kg^{-1} in fish and 220–3000 L kg^{-1} in invertebrates. As well, a recent study indicated that the BCF increased significantly at lower concentrations, up to BCF = 1260 after a 144 h exposure of zebrafish larvae to a water TBP level of 300 ng L^{-1} (Fu et al., 2020). The results showed that TBP could possibly have an unexpected high bioaccumulation potential in marine organisms at environmental levels. If such values were confirmed, TBP would be classified as very bioaccumulative (Arnot and Gobas, 2006; ECHA, 2017).

Table 2
Endpoints considered to estimate the PNEC value in seawater.

Organism	Endpoint	Level (ng L^{-1})	Ref.
Diatoms *Bacciliariaphycea* sp.	NOEC, photosynthesis	500 000	Delacroix et al. (2013)
Abalone *H. discus hannai* larvae	NOEC development 24 h	1000	Li et al. (2009)
Sea urchin *S. nudus* larvae	NOEC development 1 h	1000	Agatsuma et al. (2008)
Sea urchin *P. miliaris*	NOEC, fertility	33 000	Schäfer et al. (2009)
Sea urchin *P. lividus* larvae	NOEC, development 48 h	381 000	Lebaron et al. (2019)
Fish *D. rerio*	LOEC, reproduction 120 d	300	Deng et al. (2010)
Fish *R. quelen* larvae	LOEC, survival 96 h	300	Folle et al. (2020)
Fish *D. rerio*	LOEC, endocrine disruption	300	Fu et al. (2020)

Recent studies revealed that TBP induced acute and chronic toxic effects to freshwater adult fish *O. niloticus* after oral exposures down to 5 ng g^{-1} (Folle et al., 2021) and even 0.5 ng g^{-1} (Oliveira de Oliveira Ribeiro et al., 2021). In the present study, average levels were much higher in the tissues of marine biota from the Gulf of Fos (Table 1), thus consisting in a significant environmental risk to other organisms and suggesting that TBP contamination could extend through the whole food chain in the Gulf of Fos. On the other hand, mean levels from reference sites (Sète, Corsica, Port-Cros NP) were below 5 ng g^{-1} (Table 1). The incidence of TBP exposure on human health is still poorly documented, and a provisional oral reference dose p-RfD = 9 µg kg^{-1} d^{-1} was derived from only a single study establishing a sub-chronic exposure p-RfD based on increased serum creatinine in rats (USEPA, 2009). Considering the most contaminated organisms in the Gulf of Fos, this p-RfD value would be reached for a 70 kg adult for the consumption of 39.4 kg d^{-1} of European conger, or 13.4 kg d^{-1} of Mediterranean mussel, or 11.7 kg d^{-1} of purple sea urchin. This indicated that human health should not be affected by TBP contamination of marine biota in the industrial Gulf of Fos. However, some recent studies revealed its strong endocrine disrupting potential (Leonetti et al., 2016; Zheng et al., 2022), and cocktail effects should be considered (Lebaron et al., 2019). Therefore, further research is clearly required to refine the human toxicological values for TBP and to evaluate potential impacts to human health.

4. Conclusion

TBP was measured in marine waters, with a decreasing gradient from chlorination outlets to more distant sites, confirming the large contribution of industrial chlorination processes to the TBP levels recorded in the industrialized Gulf of Fos. The development of passive sampling was a promising method to better evaluate the dispersion of TBP. While often below detection limits in spot water analyses, the qualitative data gathered by passive sampling showed that TBP may diffuse at low levels over larger areas than previously expected.

The bioaccumulation was elevated in marine organisms from the Gulf of Fos, significantly higher than in other West Mediterranean sites, supporting the potentially harmful impacts of the overexposure to TBP induced by chlorination discharges. While interesting relations between TBP levels and physiological parameters were highlighted, the exposure and accumulation pathways remained unclear and need to be further explored. TBP appeared as potentially very bioaccumulative and its accumulation in marine biota clearly associated to the chlorination discharges in the industrial bay.

The levels recorded in European conger, purple sea urchin, and Mediterranean mussel of the Gulf of Fos were also consistent with oral toxic effects to some marine organisms, but on the basis of current knowledge, not to humans. However, the evaluation of the toxicity to humans is particularly scarce and should be reevaluated in the light of the potential risk induced by fish consumption where potential TBP sources such as chlorination discharges are expected.

Finally, further cocktail effects induced by other chlorination by-

products, but also other organic and metallic pollutants, should be explored to accurately assess the risks induced by industrial discharges to ecosystems and human health in such environments.

Declaration of competing interest

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

Data availability

Full data is made available as a \"supplementary data\" CSV file.

Acknowledgments

The authors are grateful to Sonia Ternengo (Corsica University) and STARESO staff for providing the purple sea urchin sample from Corsica. We also kindly acknowledge the boat pilots and fishermen for sharing their rich experience and for their navigation and fishing.

This work was supported by the French National Research Agency (ANR) within the project FOS-SEA (ANR-16-CE34-0009) and by the Conseil Regional Provence Alpes Côte d'Azur (Regional Council SUD-PACA).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.119742.

References

Agatsuma, Y., Endo, H., Taniguchi, K., 2008. Inhibitory effect of 2,4-dibromophenol and 2, 4, 6-tribromophenol on larval survival and metamorphosis of the sea urchin *Strongylocentrotus nudus*. Fish. Sci. 74 (4), 837–841. https://doi.org/10.1111/j.1444-2906.2008.01596.x.

Agus, E., Sedlak, D.L., 2010. Formation and fate of chlorination by-products in reverse osmosis desalination systems. Water Res. 44 (5), 1616–1626. https://doi.org/10.1016/j.watres.2009.11.015.

Ahn, Y.G., Shin, J.H., Kim, H.Y., Khim, J., Lee, M.K., Hong, J., 2007. Application of solid-phase extraction coupled with freezing-lipid filtration clean-up for the determination of endocrine-disrupting phenols in fish. Anal. Chim. Acta 603 (1), 67–75. https://doi.org/10.1016/j.aca.2007.09.045.

Allonier, A.S., Khalanski, M., Camel, V., Bermond, A., 1999. Determination of dihaloacetonitriles and halophenols in chlorinated sea water. Talanta 50 (1), 227–236. https://doi.org/10.1016/S0039-9140(99)00123-X.

Amri, S., Samar, M.F., Sellem, F., Ouali, K., 2017. Seasonal antioxidant responses in the sea urchin *Paracentrotus lividus* (Lamarck 1816) used as a bioindicator of the environmental contamination in the South-East Mediterranean. Mar. Pollut. Bull. 122 (1–2), 392–402. https://doi.org/10.1016/j.marpolbul.2017.06.079.

Andral, B., Galgani, F., Tomasino, C., Bouchoucha, M., Blottiere, C., Scarpato, A., Benedicto, J., Deudero, S., Calvo, M., Cento, A., Benbrahim, S., Boulahdid, M., Sammari, C., 2011. Chemical contamination baseline in the Western basin of the Mediterranean Sea based on transplanted mussels. Arch. Environ. Contam. Toxicol. 61 (2), 261–271. https://doi.org/10.1007/s00244-010-9599-x.

Andrisoa, A., Lartaud, F., Rodellas, V., Neveu, I., Stieglitz, T.C., 2019. Enhanced growth rates of the Mediterranean mussel in a coastal lagoon driven by groundwater inflow. Front. Mar. Sci. 6, 753. https://doi.org/10.3389/fmars.2019.00753.

Arnoldsson, K., Andersson, P.L., Haglund, P., 2012. Formation of environmentally relevant brominated dioxins from 2,4,6-tribromophenol via bromoperoxidase-catalyzed dimerization. Environ. Sci. Technol. 46 (13), 7239–7244. https://doi.org/10.1021/es301255e.

Arnot, J.A., Gobas, F.A., 2006. A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic organisms. Environ. Rev. 14 (4), 257–297. https://doi.org/10.1139/a06-005.

Bidleman, T.F., Andersson, A., Jantunen, L.M., Kucklick, J.R., Kylin, H., Letcher, R.J., Tysklind, M., Wong, F., 2019. A review of halogenated natural products in Arctic, Subarctic and Nordic ecosystems. Emerg. Contam. 5, 89–115. https://doi.org/10.1016/j.emcon.2019.02.007.

Boudjellaba, D., Dron, J., Revenko, G., Demelas, C., Boudenne, J.L., 2016. Chlorination by-product concentration levels in seawater and fish of an industrialised bay (Gulf of Fos, France) exposed to multiple chlorinated effluents. Sci. Total Environ. 541, 391–399. https://doi.org/10.1016/j.scitotenv.2015.09.046.

Cau, A., Manconi, P., 1984. Relationship of feeding, reproductive cycle and bathymetric distribution in Conger conger. Mar. Biol. 81 (2), 147–151. https://doi.org/10.1007/BF00393113.

Chen, C.E., Liu, Y.S., Dunn, R., Zhao, J.L., Jones, K.C., Zhang, H., Ying, G.G., Sweetman, A.J., 2020. A year-long passive sampling of phenolic endocrine disrupting chemicals in the East River, South China. Environ. Int. 143, 105936 https://doi.org/10.1016/j.envint.2020.105936.

Chung, H.Y., Joyce Ma, W.C., Kim, J.S., 2003. Seasonal distribution of bromophenols in selected Hong Kong seafood. J. Agric. Food Chem. 51 (23), 6752–6760. https://doi.org/10.1021/jf034632r.

Core Team, R., 2020. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/.

Dahlberg, A.K., Chen, V.L., Larsson, K., Bergman, Å., Asplund, L., 2016a. Hydroxylated and methoxylated polybrominated diphenyl ethers in long-tailed ducks (*Clangula hyemalis*) and their main food, Baltic blue mussels (*Mytilus trossulus, Mytilus edulis*). Chemosphere 144, 1475–1483. https://doi.org/10.1016/j.chemosphere.2015.10.012.

Dahlberg, A.K., Bignert, A., Legradi, J., Legler, J., Asplund, L., 2016b. Anthropogenic and naturally produced brominated substances in Baltic herring (*Clupea harengus membras*) from two sites in the Baltic Sea. Chemosphere 144, 2408–2414. https://doi.org/10.1016/j.chemosphere.2015.10.134.

Dahlgren, E., Lindqvist, D., Dahlgren, H., Asplund, L., Lehtilä, K., 2016. Trophic transfer of naturally produced brominated aromatic compounds in a Baltic Sea food chain. Chemosphere 144, 1597–1604. https://doi.org/10.1016/j.chemosphere.2015.10.024.

de Oliveira Ribeiro, C.A., Bozza, D.A., Esquivel, L., de Oliveira, E.C., Neto, F., 2021. Comparative effects of oral exposure to 2,4,6-tribromophenol and decabromodiphenyl ether in Nile tilapia. Environ. Sci. Pollut. Res. 29 (12), 17087–17102. https://doi.org/10.1007/s11356-021-16779-x.

Delacroix, S., Vogelsang, C., Tobiesen, A., Liltved, H., 2013. Disinfection by-products and ecotoxicity of ballast water after oxidative treatment–Results and experiences from seven years of full-scale testing of ballast water management systems. Mar. Pollut. Bull. 73 (1), 24–36. https://doi.org/10.1016/j.marpolbul.2013.06.014.

Deng, J., Liu, C., Yu, L., Zhou, B., 2010. Chronic exposure to environmental levels of tribromophenol impairs zebrafish reproduction. Toxicol. Appl. Pharmacol. 243 (1), 87–95. https://doi.org/10.1016/j.taap.2009.11.016.

Dron, J., Revenko, G., Chamaret, P., Chaspoul, F., Wafo, E., Harmelin-Vivien, M., 2019. Contaminant signatures and stable isotope values qualify European conger (*Conger conger*) as a pertinent bioindicator to identify marine contaminant sources and pathways. Ecol. Indicat. 107, 105562 https://doi.org/10.1016/j.ecolind.2019.105562.

ECHA (European Chemicals Agency), 2008. Guidance on information requirements and chemical safety assessment. In: Chapter R.10: Characterization of Dose [concentration]-Response for Environment. ECHA Guidance. https://echa.europa.eu/documents/10162/17224/information_requirements_r10_en.pdf/bb902be7-a503-4ab7-9036-d866b8ddce69?t=1322594768638.

ECHA (European Chemicals Agency), 2016. Substance evaluation conclusion as required by REACH article 48 and evaluation report for 2,4,6-tribromophenol. In: Substance Evaluation Conclusion Document EC No 204-278-6. https://echa.europa.eu/documents/10162/fd19d44e-7365-c189-d263-d3b0f4cc7dd9.

ECHA (European Chemicals Agency), 2017. Guidance on information requirements and chemical safety assessment. In: Chapter R.11: PBT/vPvB Assessment. ECHA Guidance. ECHA-17-G-12-EN. https://echa.europa.eu/documents/10162/17224/information_requirements_r11_en.pdf/a8cce23f-a65a-46d2-ac68-92fee1f9e54f?t=1498475968629.

Folle, N.M.T., Azevedo-Linhares, M., Garcia, J.R.E., da Costa Souza, A.T., Grötzner, S.R., de Oliveira, E.C., Paulin, A.F., Leite, N.F., Neto, F.F., de Oliveira Ribeiro, C.A., 2020. Low concentration of 2,4,6-tribromophenol (TBP) represents a risk to South American silver catfish *Ramdia quelen* (Quoy and Gaimard, 1824) population. Ecotoxicol. Environ. Saf. 187, 109815 https://doi.org/10.1093/toxsci/kfz155.

Folle Mary Turcatti, Nilce, Azevedo-Linhares, Maristela, Garcia Ramon Esquivel, Juan, Esquivel, Luise, Grotzner Regina, Sonia, de Oliveira Celton, Elton, Neto Filipak, Fransisco, de Oliveira Riveiro Alberto, Ciro, 2021. 2,4,6-Tribromophenol is toxic to Oreochromis niloticus (Linnaeus, 1758) after trophic and subchronic exposure. Chemosphere 268, 128785. https://doi.org/10.1016/j.chemosphere.2020.128785.

Fu, J., Guo, Y., Wang, M., Yang, L., Han, J., Lee, J.S., Zhou, B., 2020. Bioconcentration of 2, 4, 6-tribromophenol (TBP) and thyroid endocrine disruption in zebrafish larvae. Ecotoxicol. Environ. Saf. 206, 111207 https://doi.org/10.1016/j.ecoenv.2020.111207.

Grodtke, M., Paschke, A., Harzdorf, J., Krauss, M., Schüürmann, G., 2021. Calibration and field application of the Atlantic HLB Disk containing Chemcatcher® passive sampler–Quantitative monitoring of herbicides, other pesticides, and transformation products in German streams. J. Hazard Mater. 410, 124538 https://doi.org/10.1016/j.jhazmat.2020.124538.

Grote, M., Boudenne, J.L., Croué, J.P., Escher, B.I., von Gunten, U., Hahn, J., Höfer, T., Jenner, H., Jiang, J., Karanfil, T., Khalanski, M., Kim, D., Linders, J., Manasfi, T., Polman, H., Quack, B., Tegtmeier, S., Werschkun, B., Zhang, X., Ziegler, G., 2022. Inputs of disinfection by-products to the marine environment from various industrial activities: comparison to natural production. Water Res. 217, 118383 https://doi.org/10.1016/j.watres.2022.118383.

Heeb, M.B., Criquet, J., Zimmermann-Steffens, S.G., Von Gunten, U., 2014. Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds—a critical review. Water Res. 48, 15–42. https://doi.org/10.1016/j.watres.2013.08.030.

Hong, J., Kim, H.Y., Kim, D.G., Seo, J., Kim, K.J., 2004. Rapid determination of chlorinated pesticides in fish by freezing-lipid filtration, solid-phase extraction and gas chromatography–mass spectrometry. J. Chromatogr. A 1038 (1–2), 27–35. https://doi.org/10.1016/j.chroma.2004.03.003.

IMO, 2008. Guidelines for approval of ballast water management systems (G8). In: Resolution MEPC.174, vol. 58. International Maritime Organization, London, UK. https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/IndexofIMOResolutions/MEPCDocuments/MEPC.174(58).pdf.

Jia, X., Wang, W., Yao, Y., He, Y., Corvini, P.F.X., Ji, R., 2020. Fate of 2, 4, 6-tribromophenol in soil under different redox conditions. Bull. Environ. Contam. Toxicol. 104 (5), 707–713. https://doi.org/10.1007/s00128-020-02835-8.

Khalanski, M., Jenner, H.A., 2012. Chlorination chemistry and ecotoxicology of the marine cooling water systems. In: Rajagopal, S., Jenner, H.A., Venugopalan, V.P. (Eds.), Operational and Environmental Consequences of Large Industrial Cooling Water Systems. Springer, Boston, pp. 183–226. https://doi.org/10.1007/978-1-4614-1698-2_9.

Knudsen, G.A., Trexler, A.W., Richards, A.C., Hall, S.M., Hughes, M.F., Birnbaum, L.S., 2019. 2,4,6-tribromophenol disposition and kinetics in rodents: effects of dose, route, sex, and species. Toxicol. Sci. 169 (1), 167–179. https://doi.org/10.1093/toxsci/kfz044.

Koch, C., Sures, B., 2018. Environmental concentrations and toxicology of 2, 4, 6-tribromophenol (TBP). Environ. Pollut. 233, 706–713. https://doi.org/10.1016/j.envpol.2017.10.127.

Lebaron, K., Mechiri, L., Richard, S., Austruy, A., Boudenne, J.L., Coupé, S., 2019. Assessment of individual and mixed toxicity of bromoform, tribromoacetic-acid and 2,4,6-tribromophenol, on the embryo-larval development of *Paracentrotus lividus* sea urchin. Environ. Sci. Pollut. Res. 26 (20), 20573–20580. https://doi.org/10.1007/s11356-019-05279-8.

Leonetti, C., Butt, C.M., Hoffman, K., Hammel, S.C., Miranda, M.L., Stapleton, H.M., 2016. Brominated flame retardants in placental tissues: associations with infant sex and thyroid hormone endpoints. Environ. Health 15 (1), 1–10. https://doi.org/10.1186/s12940-016-0199-8.

Li, J.Y., Agatsuma, Y., Taniguchi, K., 2009. Inhibitory effect of 2,4-dibromophenol and 2,4,6-tribromophenol on settlement and survival of larvae of the Japanese Abalone *Haliotis discus hannai Ino*. J. Shellfish Res. 28 (4), 877–882. https://doi.org/10.2983/035.028.0417.

Löfstrand, Karin, 2011. Trends and exposure of naturally produced brominated substances in Baltic biota - with focus on OH-PBDEs, MeO-PBDEs and PBDDs. Stockholm University, p. 70. PhD thesis.

Löfstrand, K., Malmvärn, A., Haglund, P., Bignert, A., Bergman, Å., Asplund, L., 2010. Brominated phenols, anisoles, and dioxins present in blue mussels from the Swedish coastline. Environ. Sci. Pollut. Res. 17 (8), 1460–1468. https://doi.org/10.1007/s11356-010-0331-1.

Lu, Z., De Silva, A.O., McGoldrick, D.J., Zhou, W., Peart, T.E., Cook, C., Tetreault, G.R., Martin, P.A., de Solla, S.R., 2018. Substituted diphenylamine antioxidants and benzotriazole UV stabilizers in aquatic organisms in the Great Lakes of North America: terrestrial exposure and biodilution. Environ. Sci. Technol. 52 (3), 1280–1289. https://doi.org/10.1021/acs.est.7b05214.

Manasfi, T., Lebaron, K., Verlande, M., Dron, J., Demelas, C., Vassalo, L., Revenko, G., Quivet, E., Boudenne, J.L., 2019. Occurrence and speciation of chlorination byproducts in marine waters and sediments of a semi-enclosed bay exposed to industrial chlorinated effluents. Int. J. Hyg Environ. Health 222 (1), 1–8. https://doi.org/10.1016/j.ijheh.2018.06.008.

Michalowicz, Jaromir, Wluka, Anna, Bukowska, Bozena, 2022. A review on environmental occurrence, toxic effects and transformation of man-made bromophenols. Sci. Total Environ. 811, 152289 https://doi.org/10.1016/j.scitotenv.2021.152289.

Milun, V., Grgas, D., Radman, S., Štefanac, T., Ibrahimpašić, J., Landeka Dragičević, T., 2020. Organochlorines accumulation in caged mussels Mytilus galloprovincialis—possible influence of biological parameters. Appl. Sci. 10 (11), 3830. https://doi.org/10.3390/app10113830.

NCBI (National Center for Biotechnology Information), 2021. PubChem compound summary for CID 1483, 2,4,6-tribromophenol. https://pubchem.ncbi.nlm.nih%20gov/compound/2_4_6-Tribromophenol. (Accessed 12 July 2021).

Nyoni, H., Chimuka, L., Vrana, B., Cukrowska, E., Tutu, H., 2010. Optimisation of the membrane-assisted passive sampler and its comparison with solid phase extraction technique. WaterSA 36 (4). https://doi.org/10.4314/wsa.v36i4.58428.

Pérez-Palacios, T., Ruiz, J., Martín, D., Muriel, E., Antequera, T., 2008. Comparison of different methods for total lipid quantification in meat and meat products. Food Chem. 110 (4), 1025–1029. https://doi.org/10.1016/j.foodchem.2008.03.026.

Petrie, B., Gravell, A., Mills, G.A., Youdan, J., Barden, R., Kasprzyk-Hordern, B., 2016. In situ calibration of a new Chemcatcher configuration for the determination of polar organic micropollutants in wastewater effluent. Environ. Sci. Technol. 50 (17), 9469–9478. https://doi.org/10.1021/acs.est.6b02216.

Quivet, E., Hohener, P., Temime-Roussel, B., Dron, J., Revenko, G., Verlande, M., Lebaron, K., Demelas, C., Vassalo, L., Boudenne, J.L., 2022. Underestimation of anthropogenic bromoform released into the environment? Environ. Sci. Technol. 56 (3), 1522–1533. https://doi.org/10.1021/acs.est.1c05073.

Reineke, N., Biselli, S., Franke, S., Francke, W., Heinzel, N., Hühnerfuss, H., Iznaguen, H., Kammann, U., Theobald, N., Vobach, M., Wosniok, W., 2006. Brominated indoles and phenols in marine sediment and water extracts from the North and Baltic Seas–concentrations and effects. Arch. Environ. Contam. Toxicol. 51 (2), 186–196. https://doi.org/10.1007/s00244-005-0135-3.

Rocha, Filipa, Rocha, A. Cristina, Baiao F., Luis, Gadelha, Juliana, Camacho, Carolina, Carvalho, M. Luisa, Arenas, Fransisco, Oliveira, Ana, Maia R.G., Margarida, Cabrita R., Ana, Pintado, Manuela, Nunes, M. Leonor, Almeida, C. Marisa, Valente M.P., Luisa, 2019. Seasonal effect in nutritional quality and safety of the wild sea urchin Paracentrotus lividus harvested in the European Atlantic shores. Food Chem. 282, 84–94. https://doi.org/10.1016/j.foodchem.2018.12.097.

Schäfer, S., Bickmeyer, U., Koehler, A., 2009. Measuring Ca^{2+}-signalling at fertilization in the sea urchin *Psammechinus miliaris*: alterations of this Ca^{2+}-signal by copper and 2,4,6-tribromophenol. Comp. Biochem. Physiol., Part C: Toxicol. Pharmacol. 150 (2), 261–269. https://doi.org/10.1016/j.cbpc.2009.05.004.

Schlabach, M., Remberger, M., Brorström-Lundén, E., Norström, K., Kaj, L., Andersson, H., 2011. Brominated Flame Retardants (BFR) in the Nordic Environment. TemaNord 2011:528 (Nordic Council of Ministers. https://www.norden.org/en/publication/brominated-flame-retardants-bfr-nordic-environment.

Sim, W.J., Lee, S.H., Lee, I.S., Choi, S.D., Oh, J.E., 2009. Distribution and formation of chlorophenols and bromophenols in marine and riverine environments. Chemosphere 77 (4), 552–558. https://doi.org/10.1016/j.chemosphere.2009.07.006.

Steffani, C.N., Branch, G.M., 2003. Growth rate, condition, and shell shape of *Mytilus galloprovincialis*: responses to wave exposure. Mar. Ecol. Prog. Ser. 246, 197–209. https://doi.org/10.3354/meps246197.

USEPA (United States Environmental Protection Agency), 2009. Provisional peer-reviewed toxicity values for 2,4,6-tribromophenol. https://hhpprtv.ornl%20gov/issue_papers/Tribromophenol246.pdf.

Vetter, W., Kaserzon, S., Gallen, C., Knoll, S., Gallen, M., Hauler, C., Mueller, J.F., 2018. Occurrence and concentrations of halogenated natural products derived from seven years of passive water sampling (2007–2013) at Norman by Island, Great Barrier Reef, Australia. Mar. Pollut. Bull. 137, 81–90. https://doi.org/10.1016/j.marpolbul.2018.09.032.

Vrana, B., Mills, G.A., Kotterman, M., Leonards, P., Booij, K., Greenwood, R., 2007. Modelling and field application of the Chemcatcher passive sampler calibration data for the monitoring of hydrophobic organic pollutants in water. Environ. Pollut. 145 (3), 895–904. https://doi.org/10.1016/j.envpol.2006.04.030.

Whitfield, F.B., Helidoniotis, F., Shaw, K.J., Svoronos, D., 1997. Distribution of bromophenols in Australian wild-harvested and cultivated prawns (shrimp). J. Agric. Food Chem. 45 (11), 4398–4405. https://doi.org/10.1021/jf970363r.

Whitfield, F.B., Helidoniotis, F., Shaw, K.J., Svoronos, D., 1998. Distribution of bromophenols in species of ocean fish from eastern Australia. J. Agric. Food Chem. 46 (9), 3750–3757. https://doi.org/10.1021/jf980274u.

Wu, Qiong, Bouwman, Hindrik, Uren C., Ryan, van der Lingen D., Carl, Vetter, Walter, 2019. Halogenated natural products and anthropogenic persistent organic pollutants in chokka squid (Loligo reynaudii) from three sites along the South Atlantic and Indian Ocean coasts of South Africa. Environ. Pollut. 255, 113282 https://doi.org/10.1016/j.envpol.2019.113282.

Zhang, X., Robson, M., Jobst, K., Pena-Abaurrea, M., Muscalu, A., Chaudhuri, S., Marvin, C., Brindle, I.D., Reiner, E.J., Helm, P., 2020. Halogenated organic contaminants of concern in urban-influenced waters of Lake Ontario, Canada: passive sampling with targeted and non-targeted screening. Environ. Pollut. 264, 114733 https://doi.org/10.1016/j.envpol.2020.114733.

Zheng, G., Melo, L., Chakraborty, R., Klaunig, J.E., Salamova, A., 2022. Biotransformation of 2,4,6-tris (2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) can contribute to high levels of 2,4,6-tribromophenol (2,4,6-TBP) in humans. Environ. Int. 158, 106943 https://doi.org/10.1016/j.envint.2021.106943.

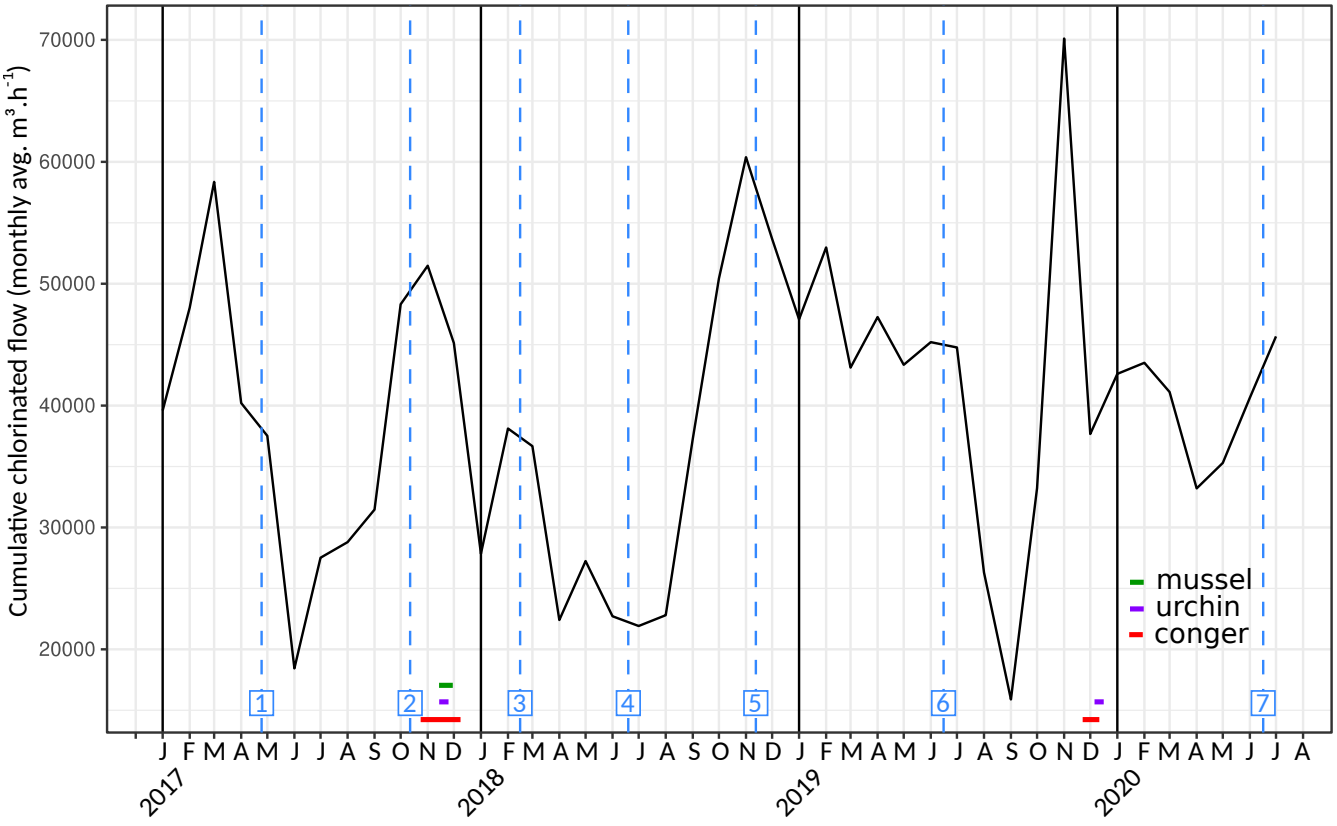
Zhou, Y., Fu, J., Wang, M., Guo, Y., Yang, L., Han, J., Zhou, B., 2023. Parental and transgenerational impairments of thyroid endocrine system in zebrafish by 2,4,6-tribromophenol. J. Environ. Sci. 124, 291–299. https://doi.org/10.1016/j.jes.2021.09.022.

Assessment of the contamination by 2,4,6-tribromophenol of marine waters and organisms exposed to chlorination discharges

SUPPORTING INFORMATION

Julien Dron, Carine Démelas, Justine Mas, Amandine Durand, Anthony Pantalacci, Annabelle Austruy, Marine Périot, Gautier Revenko, Didier Gori, Karine Lebaron, Stéphane Coupé, Patrick Höhener, Jean-Luc Boudenne

Supporting Information S1: Cumulative industrial chlorination outlets flow ($m^3.h^{-1}$) in the Gulf of Fos during the study (2017-2020). Dashed blue lines indicate the seawater spot sampling campaigns, and biota harvesting periods are also noted.



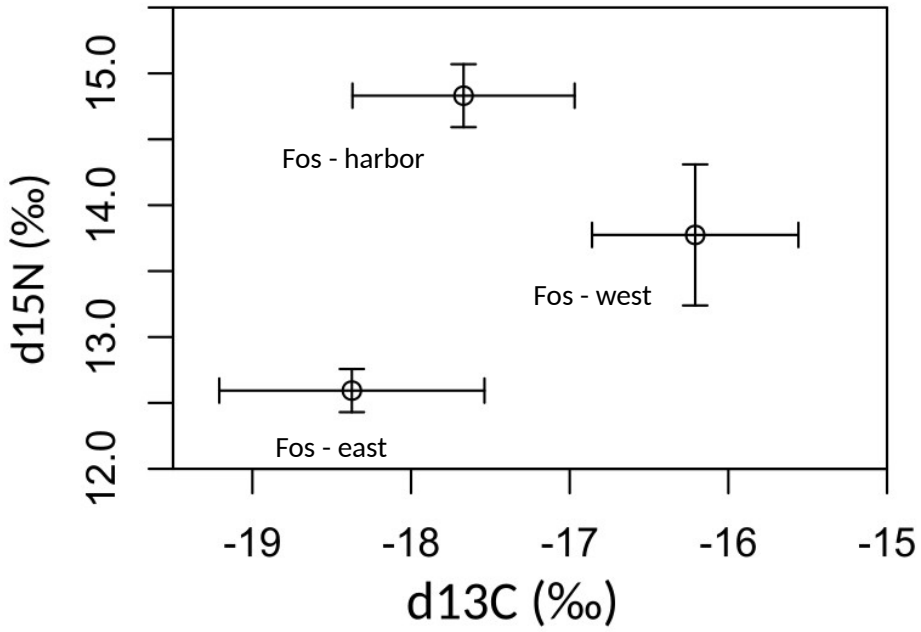
Supporting Information S2: Mean values *(standard deviations)* of the physiological characteristics of the sampled marine biota.

Specie	Location	Sampling date	Size[b] cm	Weight[b] g	Water[c] % ww	Lipid[c] % dw	N_{tot}[c] % dw	C_{tot}[c] % dw	$\delta^{15}N$ ‰	$\delta^{13}C$ ‰	*N* [a]
C. conger	Gulf of Fos	Oct-Dec 2017	105.4 *(24.9)*	2971 *(1873)*	76.9 *(1.6)*	3.68 *(1.82)*	14.1 *(0.4)*	45.4 *(1.2)*	14.67 *(0.99)*	-16.98 *(1.35)*	23
	Gulf of Fos	Nov-Dec 2019	133.0 *(17.4)*	5416 *(1956)*	78.1 *(0.8)*	5.51 *(1.25)*	14.2 *(0.5)*	46.3 *(0.7)*	15.10 *(0.29)*	-18.97 *(1.17)*	6
	Sète	Sep 2019	125.7 *(4.0)*	4931 *(786)*	76.5 *(0.7)*	5.93 *(1.85)*	14.4 *(0.2)*	47.1 *(0.4)*	12.80 *(0.20)*	-18.20 *(1.40)*	3
	Port-Cros NP	Feb 2020	117.8 *(28.8)*	4655 *(4131)*	81.0 *(2.0)*	3.75 *(0.66)*	13.9 *(0.2)*	46.0 *(0.4)*	10.40 *(0.80)*	-16.90 *(0.86)*	4
P. lividus	Gulf of Fos	Nov 2017	5.24 *(0.21)*	2.74 *(1.22)*	71.9 *(5.3)*	12.63 *(2.35)*	10.0 *(1.9)*	44.1 *(0.8)*	10.33* *(0.57)*	-17.83* *(0.87)*	6 (22)
	Gulf of Fos	Dec 2019	4.90 *(0.24)*	1.73 *(0.61)*	75.1 *(0.1)*	16.01 *(4.15)*	8.0 *(0.4)*	44.9 *(0.8)*	9.13 *(0.03)*	-18.16 *(0.57)*	1 (4)
	Calvi STARESO	Oct 2019	NA *(NA)*	NA *(NA)*	NA *(NA)*	14.52 *(NA)*	8.4 *(NA)*	44.0 *(NA)*	3.71 *(NA)*	-18.72 *(NA)*	1 (1)
	Port-Cros NP	Dec 2019	NA *(NA)*	NA *(NA)*	NA *(NA)*	23.28 *(1.79)*	8.6 *(0.1)*	43.8 *(0.4)*	4.98 *(0.23)*	-18.34 *(0.50)*	1 (2)
M. galloprov.	Gulf Fos buoys	Nov 2017	6.51 *(0.59)*	7.73 *(1.92)*	84.9 *(1.0)*	7.76 *(1.66)*	NA *(NA)*	NA *(NA)*	NA *(NA)*	NA *(NA)*	5 (15)
	Gulf Fos shore	Nov 2017	4.46 *(0.74)*	2.27 *(0.99)*	80.4 *(3.9)*	6.12 *(2.05)*	8.7 *(0.6)*	36.5 *(0.9)*	7.43* *(0.39)*	-22.20* *(0.90)*	5 (19)
	Sète farm	Mar 2020	7.28 *(0.79)*	7.30 *(1.88)*	83.2 *(1.1)*	8.04 *(1.42)*	8.9 *(0.1)*	39.3 *(0.5)*	8.13 *(0.48)*	-18.35 *(0.13)*	1 (4)
	Port-Cros NP	Mar 2020	4.33 *(0.23)*	1.16 *(0.23)*	87.0 *(1.3)*	4.82 *(0.91)*	8.6 *(0.4)*	33.4 *(0.8)*	5.56 *(0.73)*	-20.23 *(0.22)*	1 (3)

[a] Number of samples (number of subsamples). [b] Size considers C. conger whole body length, P. lividus test diameter excluding spines, and M. galloprovincialis shell length. Weight considers C. conger whole body wet weight, P. lividus gonads wet weight excluding test and spines, and M. galloprovincialis flesh wet weight excluding shell and byssus. [c] Water content refers to wet weight (% ww). Lipid, N and C total contents refer to dry weight (% dw). Only one sample (4 sub-samples) measured.*

Note on $\delta^{15}N$ and $\delta^{13}C$ results. As expected European conger (*C. conger*) appears at high $\delta^{15}N$ and $\delta^{13}C$ levels, corresponding to the top of the food web in the Gulf of Fos (Dron et al., 2019). Consistently, Mediterranean mussel (*M. galloprovincialis*) and purple sea urchin (*P. lividus*) are found at lower $\delta^{15}N$ and $\delta^{13}C$ levels. It is noteworthy that $\delta^{15}N$ values are significantly higher in the Gulf of Fos for European conger and purple sea urchin, in Fos and in the Sète farm for Mediterranean mussel. It is likely that this shift is due to the inputs of continental waters from the Rhône River, which is corroborated by higher $\delta^{13}C$ values in European conger in 2017 and purple sea urchin, as well as in the Sète mussel farm. Freshwater inputs potentially bring high quantities of suspended materials and decomposed organic matter from the continent shifting up the $\delta^{15}N$ of the whole food chain in the Gulf of Fos (and probably also in the Sète farm, Thau lagoon).

Supporting Information S3: Geographical discrimination in the Gulf of Fos on the basis of δ15N (d15N) and δ13C (d13C) levels in European conger muscles, adjusted to fish length using the linear regression equations of δ15N *vs.* fish length and δ15N *vs.* fish length, respectively (bars indicate 95% confidence intervals).



Note on $\delta^{15}N$ and $\delta^{13}C$ results. The $\delta^{15}N$ and $\delta^{13}C$ levels were adjusted to fish length, using the results of linear models as in Dron et al. (2019). The results obtained are remarkably similar to what obtained in this previous work in the same area, supporting their consistence.

Supporting Information S4: TBP concentrations (ng L^{-1}) measured in spot water sampling campaigns (sampling depth is indicated between brackets), where it was detected at least once. In other locations, not reported here, it was never detected. Mean levels were calculated considering nd = LD/2, and the outlets only when active (otherwise indicated as NA).

Site	Apr. 2017	Oct. 2017	Feb. 2018	Jun. 2018	Nov. 2018	Jun. 2019	Jun. 2020	mean
Harbor								
7p (surface)	nd	nd	nd	nd	41	nd	nd	6
7p (7 m)	nd	nd	nd	nd	41	nd	nd	6
8p (surface)	77	nd	nd	nd	41	nd	nd	17
8p (6 m)	nd	nd	nd	nd	220	nd	nd	32
Outlets								
8x2 (surface)	NA	nd	NA	nd	NA	15	NA	6
8x2 (1 m)	NA	nd	NA	580	NA	nd	NA	190
9x (surface)	nd	nd	nd	NA	nd	NA	49	11
9x (3 m)	nd	nd	nd	NA	nd	NA	88	19
10x (surface)	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*
10x (3 m)	nd*	nd*	140*	nd*	nd*	nd*	nd*	21*
11x (surface)	nd	nd	nd	NA	nd	nd	nd	nd
11x (3 m)	nd	nd	nd	NA	48	nd	nd	9
12x (surface)	nd	nd	NA	nd	nd	nd	16	4
12x (3 m)	nd	nd	NA	430	nd	5	59	84

NA: not analyzed, nd: not detected
* No information on the operating conditions of outlet 10x (steel industry)
Refer to Figure 1 for site locations and names.

Supporting Information S5: TBP concentrations (ng L^{-1}) measured in Chemcatchers® devices in June, 2019 and June, 2020, considering sampling rates R_s = 0.182 L d^{-1} (C18) and R_s = 0.050 L d^{-1} (HLB).

June, 2019 (d)	**C18**	**HLB**
17m	0.39	NA
8p	0.23	1.09
10x	NA	NA
11x	0.36	1.07
12x	0.28	1.36
June, 2020 (d)	**C18**	**HLB**
17m	NA	NA
8p	nd	0.65
10x	nd	0.55
11x	NA	NA
12x	nd	0.21

NA: not analyzed, nd: not detected

Supporting Information S6: Boxplots of the residuals of TBP levels (ng.g^{-1} lipid weight) adjusted to European conger and Mediterranean mussel length (linear fits), among locations.