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Occurrence and speciation of chlorination byproducts in marine waters and sediments of a semi-enclosed bay exposed to industrial chlorinated effluents

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ABSTRACT

Chlorination of seawater is one of the most effective technologies for industrial biofouling control. However, chlorination leads to the formation of halogenated chlorination byproducts (CBPs) associated with potential risks to environmental and human health. The present study investigated the occurrence and distribution of CBPs in the Gulf of Fos, a semi-enclosed bay where chlorinated effluents of multiple industrial plants are discharged. Seawater samples (surface and bottom) were collected at 24 sampling stations, with some near industrial outlets and others dispersed throughout the bay. Sediment samples were also collected at 10 sampling stations. Physicochemical parameters including water temperature, pH, salinity, bromide content, and free and total residual oxidant were determined. Several chemical classes of CBPs including trihalomethanes, haloacetic acids, haloacetonitriles, trihaloacetaldehydes, and halophenols were analyzed. Bromoform was the most abundant CBP in seawater, and it was detected at most of the sampling stations of the bay with highest concentrations occurring near the industrial effluent outlets. Dibromoacetic acid was the second most abundant CBP at most of the sites followed by dibromoacetonitrile. Other detected CBPs included tribromoacetic acid, bromochloroacetonitrile, and bromal hydrate. To our knowledge, the concentration of the latter CBP was reported here for the first time in the context of industrial seawater chlorination. In sediments, two bromine-containing halophenols (2-chloro-4-bromophenol and 2,4,6-tribromophenol) were detected at two sampling stations. Ecotoxicological assays and risk assessment studies based on the detected environmental concentrations are warranted to elucidate the impacts of marine CBP contamination.

1. Introduction

The use of seawater in industrial cooling or heating is a common practice in many parts of the world. One of the primary operational problems of using seawater in such processes is biofouling, which results from the growth of microorganisms (biofilms) and macro-organisms (e.g., clams) on the surface or inside industrial equipment. Biofilms tend to stick to heat-exchange surfaces, thereby significantly reducing heat-transfer coefficients, while excessive development of macro-organisms can plug heat exchangers. There are several techniques for preventing both types of biofouling. Chlorination of seawater is among the most commonly used antibiofouling treatments (Khalanski and Jenner, 2012). Chlorine is added into seawater either in the gaseous form or in the aqueous form of sodium hypochlorite solution, typically at doses of 0.5–1.5 mg/L (expressed as Cl_2) (Allonier et al., 1999a,b; Ma et al., 2011; Khalanski and Jenner, 2012). In seawater, chlorine reacts with organic and inorganic compounds leading to the formation of chlorination byproducts (CBPs) (or disinfection byproducts, DBPs) (Heeb et al., 2014). Several factors including initial chlorine dose, temperature, pH, constitution of seawater and presence of contaminants (natural or anthropogenic) can influence these reactions, leading to differences in the nature and levels of the formed CBPs (Allonier et al., 1999b; Heeb et al., 2014).

The release of chlorinated seawater into the environment constitutes a concern from environmental and human health standpoints. Chemical hazards associated with chlorination of seawater can be divided into acute effects from the action of strong oxidants and long-term effects caused by CBPs. While the employed oxidants generally act

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as corrosives on marine fauna and flora, the generated mixtures of CBPs present far more complex toxicological challenges, to both natural biota and human health (Werschkun et al., 2014). Although data on the ecotoxicity of CBPs are very limited, existing data show that persistent CBPs may induce adverse effects on marine organisms, when present above certain concentrations (Taylor, 2006; Deng et al., 2010; Pignata et al., 2012; Khalanski and Jenner, 2012). CBPs have been found to induce developmental toxicity to marine Polychaete *Platynereis dumerilii* (Yang and Zhang, 2013) and oysters *Crassostrea virginica* (Stewart et al., 1979). Data about the toxicity (with endpoints relevant to human health) of CBPs in chlorinated drinking water and swimming pool waters are much more extensive than ecotoxicity data (endpoints relevant for environmental health). Extensive studies have shown that CBPs can induce a range of adverse effects including mutagenicity, genotoxicity, and carcinogenicity (Richardson et al., 2007; Manasfi et al., 2017b). Concerns about potential human exposure to CBPs in the context of seawater chlorination are not only related to the exposure of workers in the vicinity of industrial seawater chlorination sites (Banerji et al., 2012), but also to the general population as certain persistent CBPs may potentially bioaccumulate in exposed marine organisms which are consumed as food products (e.g., fish and mussels) (Khalanski and Jenner, 2012; Boudjellaba et al., 2016). The bioaccumulation potential of an organic compound depends on its ability to accumulate in fats of marine organisms. Hence, CBPs having a high octanol/water partition coefficient (Log K_{ow}) such as 2,4,6-tribromophenol (Log $K_{ow} = 3.92–4.02$) are susceptible to bioaccumulation and have been previously detected in marine organisms (Khalanski and Jenner, 2012; Boudjellaba et al., 2016).

The identification of dominant CBPs discharged into the receiving marine waters and their concentrations is key for performing environmental and human health risk assessment. To date, there have been few studies documenting CBPs concentrations in chlorinated industrial effluents and receiving marine waters. Most of the previous studies focused on measuring a limited number of CBPs in cooling effluents of nuclear and thermal power plants and in a few discharge points in the open coast (Jenner et al., 1997; Allonier et al., 1999a,b; Khalanski and Jenner, 2012). Data about the dissemination of CBP contamination of seawater and marine sediments exposed to multiple industrial chlorinated effluents remain very scarce. Boudjellaba et al. (2016) previously explored the occurrence of CBPs in seawater and fish in the Gulf of Fos in Southeastern France, based on sampling campaigns in winter and summer 2014. The Gulf of Fos is a semi-enclosed bay that favors water confinement in some of its back-ends and receives the plumes of the second greatest Mediterranean river, namely the Rhône river, among other freshwater inputs (Ulses et al., 2005). This gulf hosts the largest port of trade in France (Marseille-Fos Port) and a major industrial zone that includes steel, petrochemical, waste incineration, and cement industries, along with gas and electricity power plants. Despite these industrial activities, amateur and professional fishing are practiced in the bay, and recreational swimming areas are also available at some coastal areas around the bay. In the study of Boudjellaba et al. (2016), CBP classes which have been previously detected in cooling water effluents were analyzed. The present study aims at conducting a more comprehensive survey about the contamination of the Gulf of Fos, by analyzing a broader array of CBPs and by sampling a more extended geographical zone to further evaluate the CBP contamination of seawater throughout the Gulf. Additionally, marine sediments were sampled to evaluate their contamination by CBPs, for the first time to our knowledge. Here, the sampling campaign was carried out during the spring season, unlike the previous survey of Boudjellaba et al. (2016). Measuring CBP concentrations in seawater during different seasons contributes to documenting their levels under different meteorological conditions (especially temperature) and potentially different chlorination practices performed by the industries in different meteorological conditions. For example, when water temperature is low some industries decrease chlorination as the risk of biofouling decreases at lower temperatures. Documenting sufficient data about the contamination of seawater by CBPs based on multiple surveys performed during different periods of the year would contribute to a better monitoring of the contamination and to defining trends, which are of high utility for risk assessment studies.

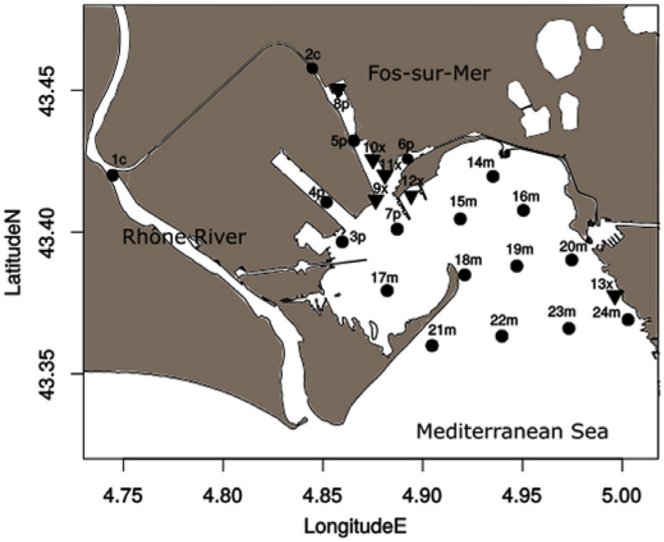

Fig. 1. Overview of the Gulf of Fos and the different sampling stations (from 1c to 24m). Triangles represent industrial effluent discharge points.

To this end, the present study investigated the contamination of seawater and sediments by CBPs in the Gulf of Fos. Several classes of halogenated CBPs including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), trihaloacetaldehydes (THA), and halophenols (HPs) were analyzed in seawater and marine sediments obtained from the vicinity of the industrial effluents and at other sites throughout the bay. Global physicochemical parameters such as temperature, pH, salinity, bromide concentration, total organic carbon (TOC), total nitrogen (TN), total oxidant residual, and free oxidant residual were also determined.

2. Materials and methods

2.1. Study site

The study investigated the Gulf of Fos (Fig. 1), which hosts numerous industrial sites. The Gulf is located in Southeastern France on the Mediterranean at about 50 km from the city of Marseille. Average water depth in the Gulf is about 20 m. The Gulf receives several freshwater inputs including a main input from the Rhône River, and minor inputs from the Berre Lagoon, irrigation and navigation canals. The region is characterized by frequent and strong north or northwest winds (around 40% per year) and southeast winds (10–20% per year). The north or northwest wind is most common in winter and spring, although it occurs in all seasons (MeteoFrance). A wind rose showing wind distributions based on normalized data from 2002 to 2011 is presented in SI (Fig. S2). Various heavy industrial activities are established around the Gulf including two large liquefied natural gas (LNG) terminals (Fos-Cavaou and Fos-Tonkin designated by sampling stations 12x and 8p, respectively). These two LNG terminals discharge chlorinated waters at a flow of 30,000 m^3/h and 15,000 m^3/h following electrochlorination or addition of sodium hypochlorite, respectively. In addition, there are other power plants which are irregularly active (designated by sampling stations 9x and 11x) which discharge chlorinated water (by electrochlorination). Metal industry (sampling station 10x) and oil refineries (sampling station 13x) also discharge chlorinated seawater at flows exceeding 10,000 m^3/h. The outlets of the different industrial sites in the Gulf of Fos are shown in Fig. 1 (sampling station names end with x and are represented in triangles). Maps of the study site were produced using R (R Core Team, 2015) and Inkscape (2015) software.

2.2. Sample collection

The sampling campaign was performed during spring (24, 25, and 26 April 2017). The different sampling stations were disseminated throughout the Gulf of Fos and included the main industrial outlets (Fig. 1). Water samples were collected at all the 24 sampling stations at the surface (depth between 0 and 50 cm) and at 7 m depth (or the bottom at the stations where the bottom is at depth < 7 m) using a 5-L Niskin bottle (General Oceanics, USA). For the analysis of CBPs, sample aliquots (1 L) were placed in amber glass bottles, ascorbic acid was rapidly added, and bottles were sealed with PTFE-lined screw caps. These CBP samples were filled without headspace to avoid any loss due to volatilization. For the analysis of global physicochemical parameters including bromide ion concentration, TOC, TN, and determination of free and total chlorine, sample aliquots (1 L) were placed in amber glass bottles with PTFE-lined screw caps to which no ascorbic acid was added. Samples were stored at 4 °C away from sunlight and extracted within 24 h from collection. Physicochemical parameters including pH, temperature, and salinity were determined on-site using a CTD-type multi-parameter probe (MS5, OTT Hydrolab, Germany). For quality control, field blanks, laboratory blanks, and laboratory-fortified blanks were sampled. Procedural standard calibration was performed using spiked seawater calibration standards, which were treated exactly in the same manner as samples. Internal standards were added to samples and used as surrogates to monitor the reliability of complete analytical procedures. A set of at least seven laboratory spiked standard solutions were analyzed to calculate the mean recovery (R) and the relative standard deviation (RSD) (Table S1). The detection limits (DL) and the quantification limits (QL) for the analyzed chemicals and parameters and their estimation procedures are presented in supplementary information (Table S1).

Sediments were collected using an Ekman grab sampler at 10 sampling stations (8p, 11x, 12x, 13x, 14m, 15m, 17m, 19m, 22m, 24m) at depths indicated in supplementary information (Table S4). The collected sediments were stored at 4 °C away from sunlight.

2.3. Chemical standards

Analytical standards including THM calibration mix, halogenated volatile mix (containing HANs), and HAA esters calibration mix, 2,3-dibromopropionic acid solution, and the THA chloral hydrate were purchased from Supelco (USA). The brominated THA tribromoacetaldehyde (97%) was purchased from Aldrich (United Kingdom) and was used to generate its hydrated form bromal hydrate (BH) in ultrapure water (Millipore, resistivity > 18 MΩ cm). HPs 2-bromo-4-chlorophenol (98%) and 2,6-dibromophenol (99%) were purchased from Alfa Aesar (Germany), and 2,4-dibromophenol (95%) and 2,4,6-tribromophenol (99%) were purchased from Sigma-Aldrich (USA). A standard stock solution of each compound was prepared in methyl *tert*-butyl ether (MTBE, purity 99.8%) which was purchased from Merck (Germany). L-ascorbic acid, crystalline, reagent grade was purchased from Sigma (China). Sulfuric acid, analytical grade reagent, was purchased from Fisher Scientific (UK). For plotting the calibration curve, artificial seawater was spiked with the mother solutions at different concentrations and the resulting solutions were treated according to the methods described hereby for samples. Artificial seawater (ASW) was prepared according to ASTM D1141-98 (2013).

2.4. Seawater sample preparation

For the analysis of THMs, HANs, THAs sample aliquots (50 mL) were first adjusted to a pH value ranging between 4.5 and 5.5 by adding sulfuric acid according to U.S. EPA Method 551 .1 with slight modifications (Munch and Hautman, 1995). Internal standards were added as surrogates to monitor the efficiency of sample treatment, and Na_2SO_4 (16 g) was then added. 1,2,3-trichloropropane was added as surrogate for the analysis of THMs, HANs and BH. Samples were extracted by liquid-liquid extraction (LLE) by adding MTBE (5 mL) and shaking manually for 3 min. Then, the organic phase was collected for analysis. For the analysis of HAAs, U.S. EPA Method 552.3 was used with slight modifications (Domino et al., 2003). In brief, sample aliquots (40 mL) were acidified to a pH < 1 by adding concentrated sulfuric acid and extracted with MTBE (4 mL). 2,3-dibromopropionic acid was added to the extracts as a surrogate. After LLE, the organic phase containing the HAAs was collected and transferred into 15 mL vials to which acidified methanol was added and placed in a water bath at 50 °C for 2 h for derivation (methylation). The vials were then cooled, and 4 mL of saturated sodium bicarbonate solution were added before collecting the organic phase containing the HAA esters in chromatographic vials. For the analysis of HPs, derivation (acetylation) and extraction by LLE were conducted as described previously by Allonier et al. (1999a) with some modifications. In brief, 50 mL samples were mixed manually during 4 min with 10 g of sodium carbonate and 5 mL of acetic anhydride to derivatize the HPs. Samples were then extracted with 2.5 mL of MTBE containing the internal standard 2,4,6 trichlorophenol. The organic phases were then collected and dried with sodium sulfate before analysis.

2.5. Analytical methods

Free residual oxidants and total residual oxidants were measured by the colorimetric DPD method using a portable spectrophotometer (AQUALYTIC-AL 800, Germany). Bromide levels in water were measured by an ICS-3000 Dionex ion chromatography system using a 30 mM NaOH eluent with a flow rate of 1.5 mL/min at 30 °C. Total Organic Carbon (TOC) and Total Nitrogen (TN) were measured using high temperature catalytic oxidation technique (Multi N/C 2100, Analytik Jena, Germany). Pre-treated samples were injected (50 μl) into the furnace filled with a Pt preconditioned catalyst. Combustion was realized at 800 °C and combustion products were carried by high purity oxygen (Linde Gas) allowing detection of CO_2 by non-dispersive infrared (NDIR) and detection of NO by chemiluminescence (CLD).

Organic extracts containing CBPs were analyzed using a gas chromatograph coupled to a ^{63}Ni electron-capture detector (GC-ECD model Clarus 580, Perkin Elmer, Norwalk, CT, USA). An Elite 5MS capillary column was used for the separation. Helium 5.0 was used as a carrier gas at 1 mL/min. Nitrogen was used as a make-up gas at 30 mL/min. For the analysis of THMs, HANs, HPs and BH the temperature program was as follows: initially 35 °C increasing to 145 °C at a rate of 10 °C/min, then at a rate of 20 °C/min up to 225 °C and finally at 10 °C/min to 260 °C, held for 2 min. For the analysis of HAAs, the temperature was initially set to 40 °C, then increased to 75 °C at a rate of 15 °C/min, then increased to 100 °C at 5 °C/min, and finally temperature reached 135 °C at 10 °C/min which and held 2 min. Analytes were qualified using procedural standard calibration. Calibrations were performed at concentrations starting from as low as 10 ng/L up to 20 μg/L, depending on the analytes (Table S1). At each concentration order, external calibrations were performed using a set of 7 standard solutions. The solutions were prepared by adding aliquots of the standard stock solution in artificial seawater, which was then treated exactly as a sample. Seawater and purified water reagent blanks were included with each sequence All analytical method validation parameters are presented in Table S1.

2.6. Sediment sample preparation

Sediments were brought to room temperature. Extraneous material was removed prior to homogenization. Sediment samples were homogenized in pre-cleaned collection jars by stirring vigorously with stainless steel spatulas. Dry weights were determined by placing sample aliquots in an oven at 105 °C and weighed at intervals of 24 h until successive weight differences became less than 4%. For the analysis of HPs in sediments, the method was inspired from Lampi et al. (1992) with modifications. An aliquot (20 g) of wet sediments was weighed, and 50 mL of 1M NaOH solution and internal standard (50 µL) of 2,4,6-trichlorophenol solution (1 mg/L) were added. Then, 50 mL of hexane were added to the sample and the whole kept in an ultrasonic bath for 10 min. The hexane phase was then discarded, and the aqueous phase was collected and introduced into 65-mL glass vials with PTFE-lined screw caps which were centrifuged at 2000 rpm for 10 min. 40 mL of the resulting supernatant was then collected and was treated according to protocols used for the analysis of HPs in water samples described above.

3. Results and discussion

3.1. Physicochemical parameters

Water quality parameters can influence the formation and decay of CBPs (Cimetiere et al., 2010; Hansen et al., 2012; Zhang et al., 2013). At the different sampling stations, physicochemical parameters including water temperature, pH, salinity, bromide concentration, TOC, TN, free residual oxidant, and total residual oxidant were determined in surface and bottom (or 7 m deep) seawater (Table S2).

Very little pH variation was observed among the different sampling points located throughout the Gulf, with pH ranging between 8.13 and 8.25 (Table S2). Water temperatures at the sampling stations close to the shore were slightly higher than at offshore stations (Fig. 2), which is likely related to the discharge of heated seawater effluents by the industrial sites. Additionally, at sampling stations near the outlets (9x, 10x, 11x), water temperatures were slightly higher at the surface than at the bottom (up to 18.9 °C and 19.8 °C, respectively) (Table S2). At offshore stations away from industrial outlets, water temperatures were globally homogeneous at the bottom and surface (around 14.5 °C), which is compatible with the agitated conditions that favor the mixing and homogenization of water bodies.

With regard to salinity, very minor variations were observed among the sampling stations located away from the shore (Fig. 1S). In contrast, near the shore, a marked influence of the Rhone River freshwater intrusion appeared at nearby stations 2c, 8p and 5p, which had lower salinities than the sampling stations located offshore. The sampling station 2c located on the canal receiving water of the Rhône River, had unusually high salinities (24.2 and 34.2 g/L on the surface and bottom, respectively). This salinity likely resulted from the vigorous mixing of the Rhône River freshwater with seawater entrained from the Gulf of Fos by the moderate to strong southeast winds registered on the day of sampling. During the sampling campaign, sustained southeast wind (35–40 km/h on average) with gusts were reported (MétéoFrance, Istres). Like salinity, bromide concentrations varied very little amongst most of the sampling stations (Fig. 3) and were generally high at the all of the sampling stations located in the Gulf (Table S2).

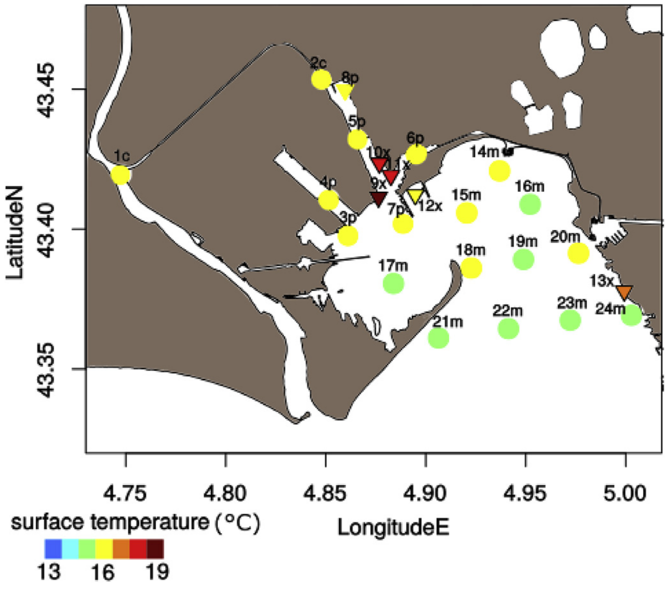

Fig. 2. Variation of surface water temperature (in °C) at the different sampling stations.

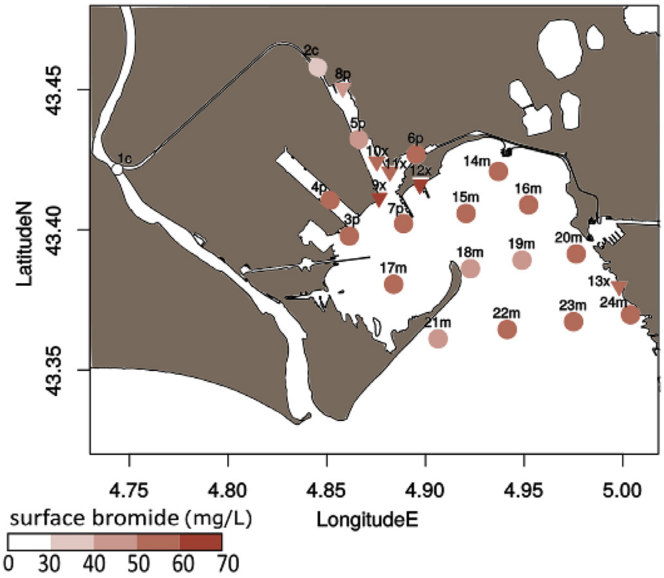

Fig. 3. Variation of surface bromide concentrations (in mg/L) at the different sampling stations. Triangles represent industrial effluent discharge points.

Total residual oxidant and free residual oxidant were not detected at any of the sampling stations. A number of factors could be at the origin of this finding including low initial chlorination level, high organic matter concentrations and temperatures (Brown et al., 2011). However, since the organic content in water (measured by TOC) and temperature were not unusually high (Table S2), the main factor is likely related to low chlorination practiced by the industries during the sampling period.

3.2. Occurrence of chlorination byproducts (CBPs) in seawater

The levels of the CBPs measured at all the sampling stations are presented in Table S3. Fig. 4 summarizes the sampling stations at which CBPs were measured (whether on the surface or in the bottom) at levels higher than QL. These CBPs were all brominated including bromoform, dibromoacetic acid (DBAA), dibromoacetonitrile (DBAN), tribromoacetic acid (TBAA), and BH. Low concentrations of bromochloroacetonitrile (BCAN) were also detected near some outlets (sampling stations 8p, 9x, and 10x) (Table S3). In previous studies of chlorinated cooling waters, CBPs including THMs, HAAs, HANs, and HPs have been detected (Khalanski and Jenner, 2012), but to our knowledge, this is the first study to report the occurrence of BH (hydrated form of tribromoacetaldehyde), in the context of industrial seawater chlorination. Nevertheless, BH has been previously detected in chlorinated seawater pools and in bromide-rich drinking waters (Krasner et al., 2006; Manasfi et al., 2017c).

The occurrence of predominantly brominated CBPs in chlorinated seawater is in agreement with previous studies that explored the formation of CBPs in chlorinated seawater (Jenner et al., 1997; Allonier et al., 1999b; Boudjellaba et al., 2016). This speciation can be explained

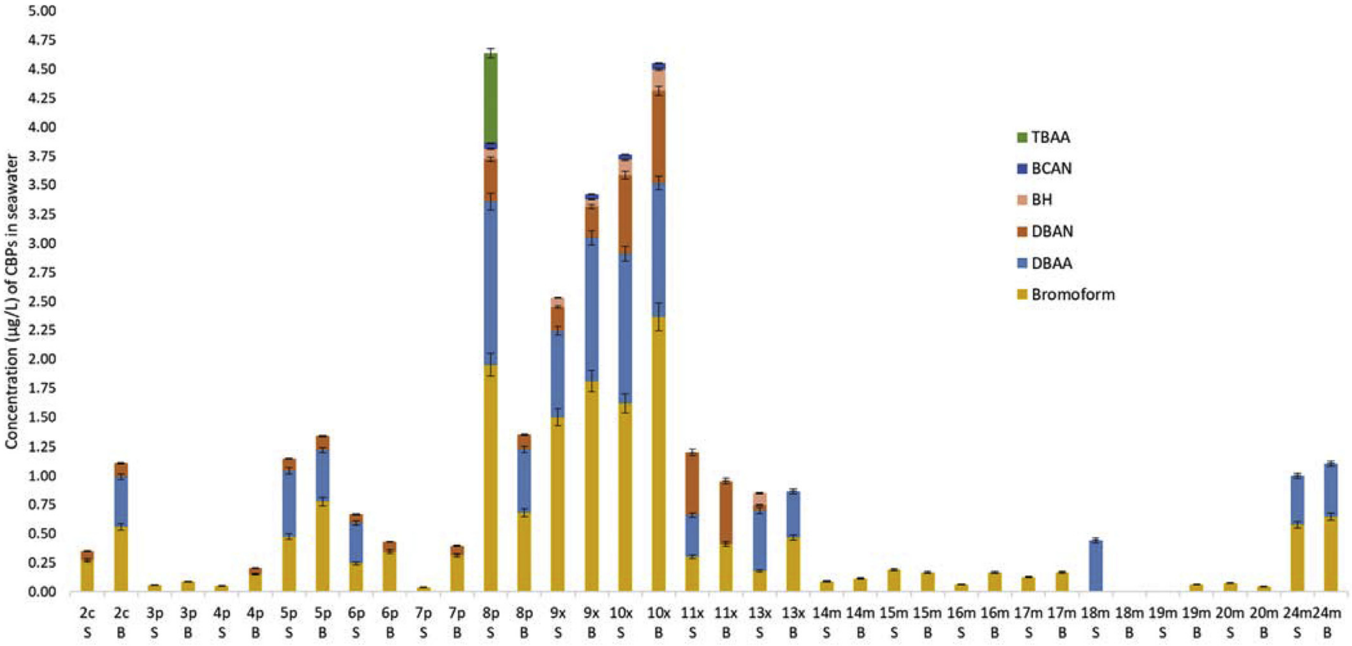

Fig. 4. Concentrations of CBPs at sampling station where CBPs > QL were detected. B represent Bottom samples and S represents Surface samples. TBAA: tribromoacetic acid; BCAN: bromochloroacetonitrile; BH: bromal hydrate; DBAN: dibromoacetonitrile; DBAA: dibromoacetic acid. Errors bars are based on RSD% of CBPs.

by the formation of bromine upon the addition of chlorine to seawater, which contains elevated bromide concentrations known to enhance the formation of brominated CBPs (Hua et al., 2006). In the presence of appreciable amounts of bromide ions, chlorine oxidizes bromide ions and forms hypobromous acid and hypobromite ions (Singer, 1999). As an oxidant, bromine is stronger than chlorine and reacts 10 times faster with organic matter (Westerhoff et al., 2004). The reactions leading to the formation of bromine in bromide-rich water such as seawater are as follows (Heeb et al., 2014):

$$HOCl + Br^{-} \rightarrow HOBr + Cl^{-} \; k_1 = (1.55\text{–}6.84).10^{3}\,M^{-1}\,s^{-1} \quad (1)$$

$$ClO^{-} + Br^{-} \rightarrow BrO^{-} + Cl^{-} \; k_2 = 9.10^{-4}\,M^{-1}\,s^{-1} \quad (2)$$

Although HOBr and OBr^{-} are the most abundant species involved in these reactions, several bromine species can react with organic compounds present in seawater (Heeb et al., 2014; Manasfi et al., 2017a,b). Bromine species such as Br_2, Br_2O, BrOCl, and BrCl are less abundant but more reactive than HOBr and OBr^{-} and have been shown to contribute to the bromination of some organic compounds (Sivey et al., 2013). Table 1 shows the equilibrium concentrations of bromine species when seawater containing 58 mg/L bromide, at pH 8.2, is chlorinated at 1 mg/L active chlorine. These concentrations were estimated using PHREEQC (Parkhurst and Appelo, 2013).

Table 1
Molar concentrations of bromine species at equilibrium in seawater (Bromide 58 mg/L; 20 g/L chloride, pH 8.2; chlorinated with 1 mg/L active chlorine), calculated using PHREEQC (Parkhurst and Appelo, 2013).

Bromine Species	Concentration (M)
HOBr	1.70×10^{-5}
OBr^{-}	1.04×10^{-5}
Br_2	7.62×10^{-9}
Br_2Cl^{-}	5.10×10^{-9}
Br_2O	2.10×10^{-9}
BrCl	2.38×10^{-10}
Br_3^{-}	8.18×10^{-11}
$BrCl_2^{-}$	7.98×10^{-11}
BrOCl	5.33×10^{-13}

The levels of CBPs were highest at the sampling stations located near the outlets where chlorinated industrial effluents are released (stations 8p, 9x, 10x, 11x, and 13x) (Fig. 4). At these outlets, the concentration of bromoform reached 1.95 µg/L at the surface and 2.36 µg/L at the bottom (Table S3). The slightly higher concentrations of bromoform at the bottom compared to the surface may result from accelerated volatilization on the surface because of wind and the slightly higher temperatures. For the other CBPs, such distinctive discrepancies between bottom and surface levels were not observed. DBAA, which was the second most abundant CBP, reached 1.40 µg/L at station 8p (surface). DBAN had a maximal concentration of 0.79 µg/L at station 10x. At the sampling station 12x (in the vicinity of the outlet of LNG Fos-Cavaou terminal), concentrations of CBPs were unexpectedly low compared to the other stations near effluent discharges. This aberration is probably due to the dislocation of the sampling Niskin bottle under the effect of wind during sampling. Strong southeast winds and currents made sampling very difficult at this station, located at about 150 m from the shore. At sampling stations distant from the outlets of industrial effluents such as 14m, 15m, 16m, 17m, only bromoform was still detected at levels above the QL (Fig. 5). For example, at stations 14m, 15m, 16m, bromoform concentration was 0.16 µg/L. However, these bromoform concentrations at the offshore stations are still superior to typical background levels of bromoform found in seawater (emitted by marine algae) unexposed to chlorinated effluents. Bromoform background levels have been estimated at 0.025 µg/L, and rarely exceed 0.1 µg/L unless when extensive beds of macro-algae are present, which is not the case in the Gulf of Fos (Quack and Wallace, 2003). Thus, these above-background concentrations can be attributed to the release of CBPs from industrial sites into the gulf.

In a previous survey, Jenner et al. (1997) investigated the occurrence of CBPs in cooling water of several coastal power stations located in the UK, France, and the Netherlands. The analyzed CBPs included THMs, HANs, and HPs. Among these CBPs, bromoform and dibromoacetonitrile (DBAN) were the main detected compounds in power stations effluents at concentration that ranged from 0.72 to 29.20 µg/L, and from < 0.1 to 3.15 µg/L, respectively (Jenner et al., 1997). Moreover, Allonier et al. (1999b) measured THMs, HANs, HPs and HAAs in

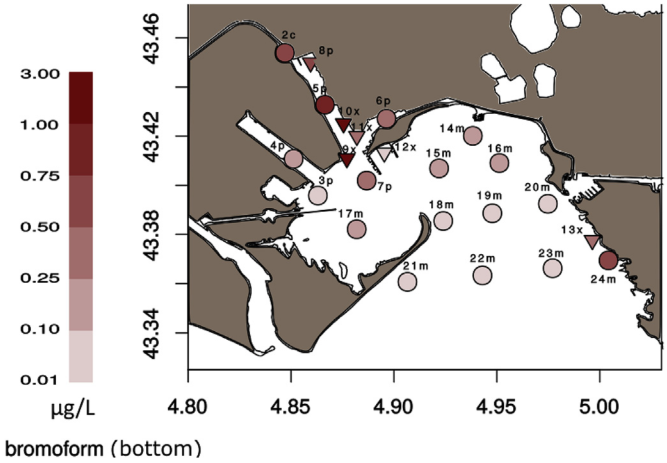

Fig. 5. Bromoform concentration (in µg/L) in bottom seawater at the sampling stations. Triangles represent industrial effluent discharge points.

effluents of three French nuclear power stations after on-site chlorination. The major compound formed in all power stations was bromoform at concentrations that ranged from 1.66 to 26.80 µg/L. DBAA and DBAN were also detected at levels ranging from 1.96 to 10.19 µg/L and from 0.94 to 3.61 µg/L, respectively. Accordingly, the levels of CBPs reported in these previous investigations of power station cooling water effluents were higher than levels reported in the present study. However, it should be noted that the maximal concentrations reported in those previous studies of power station effluents were detected in the chlorinated effluents themselves, unlike in the current study where the contamination of the receiving seawater at sampling stations dispersed inside the Gulf is explored, by measuring CBPs in the Gulf seawater instead of the effluents themselves. Furthermore, in these previous studies total residual oxidant ranged from 0.3 to 1.5 mg/L (Jenner et al., 1997) and from 0.2 to 0.77 (Allonier et al., 1999b), suggesting stronger chlorination than what was practiced in the Gulf of Fos where total residual oxidant levels were below QL (Table S2). A correlation between residual oxidant levels and CBP concentrations has been previously suggested in previous studies of power station cooling effluents, with lowest CBP concentrations being detected at lowest total residual oxidant levels.

By comparing the findings of the present study conducted in spring season with the findings of the previous survey of Boudjellaba et al. (2016) conducted in the Gulf of Fos in winter and summer seasons, a discrepancy appears between CBP levels in summer compared to those in spring or winter which were quite similar. In the previous survey of Boudjellaba et al. (2016), the used analytical methods had higher DLs and QLs resulting in undocumented levels for many of the analyzed CBPs at most of the sampling stations, as reported by authors. Therefore, the description of variation of CBP contamination among different seasons can be chiefly performed by comparing the concentrations of bromoform as it represented the most detected CBP in the past and present surveys. In Boudjellaba et al. (2016), bromoform concentrations in surface seawater reached 2.51 µg/L and 7.55 µg/L in winter and summer, respectively, with highest concentrations detected near outlets. Other CBPs such as HAAs were only detected in summer with DBAA reaching 2.20 µg/L at the surface. In the present study, bromoform concentration in surface seawater reached 1.95 µg/L, and DBAA concentration reached 1.40 µg/L. Hence, it appears that the contamination of the Gulf of Fos by CBPs was highest in summer. This finding is likely related to variations of industrial chlorination treatments as a function of water quality parameters especially temperature, which differ from one season to another. In summer, high water temperature (22–23 °C) would favor bacterial and algal development which leads industries to increase chlorination to face the elevated biofouling risks as compared to lower risks in colder seasons. In spring and winter, differences in bromoform concentration appear to be very minor. It should be noted that the water temperatures were also very similar: 14.5 °C in spring campaign reported here, and 13 °C in winter campaign reported in Boudjellaba et al. (2016), which could result in similar chlorination practices performed by the industrial sites in these similar conditions.

Overall, the levels of CBPs measured in the Gulf were relatively low. Yet, although these low concentrations are not expected to constitute a threat to human health via direct exposure, concerns regarding potential ecotoxic effects and the accumulation of CBPs in seafood (thus indirect human exposure) cannot be dismissed, especially that CBPs are discharged into seawater in a chronic manner. Additionally, the brominated speciation of the detected CBPs contributes to these concerns, since brominated CBPs are known to be far more toxic than their chlorinated analogues (Richardson et al., 2007). Furthermore, the existence of a potential cocktail effect where the overall toxicity of CBPs is accentuated due to additive or synergistic interactions among different contaminants could also be an aggravating factor (Banerji et al., 2012).

3.3. *Distribution of CBPs in seawater*

Among the detected CBPs, bromoform was the most abundant species at most of the sampling stations (Fig. 6). This finding is in agreement with previous studies that investigated the occurrence of CBPs in seawaters exposed to chlorinated industrial effluents (Jenner et al., 1997; Allonier et al., 1999b; Boudjellaba et al., 2016). DBAA was the second most abundant CBP at all the sampling sites except station 11x where DBAN constituted the second most abundant species. This discrepancy can be attributed to the presence of nitrogen-containing organic compounds near the industrial outlet 11x. Unlike DBAA, the tribrominated HAA, TBAA, was detected only at the sampling station 8p. This finding may be explained by the lower stability of TBAA in comparison to DBAA (Zhang and Mineara, 2002; Manasfi et al., 2016). It has been reported that TBAA may decompose to form bromoform in aqueous solutions (Zhang and Mineara, 2002). HPs were not detected in seawater samples.

The distribution of CBPs observed here (THM most dominant followed by HAAs) is similar to the distribution observed in chlorinated drinking water but distinct from that found in chlorinated swimming pools, where HAAs represent the most dominant DBPs followed by THMs (Chowdhury et al., 2014). The discrepancy between these distributions is related to the nature of precursors leading to the formation of CBPs. In seawater and drinking water, NOM represent the main organic precursors, while in swimming pools anthropogenic inputs are the main precursors. In a previous investigation (Kanan and Karanfil, 2011), NOM were found to contribute mostly to the formation of THMs, while anthropogenic precursors (body fluids) contributed mostly to the formation of HAAs. Although this highlights the role of NOM in the formation of CBPs detected in the Gulf of Fos, the contribution of other types of precursors (e.g. synthetic organic compounds from industrial sites) can't be dismissed based on this observation.

3.4. *Occurrence of brominated halophenols in sediments*

Marine sediments were collected at the sampling stations (8p, 11x, 12x, 13x, 14m, 15m, 17m, 19m, 22m, 24m). Two bromine-containing HPs were detected at the sampling stations 22m and 13x at concentrations in the order of ng/g dry weight. At sampling station 22m, 2-chloro-4-bromophenol and 2,4,6-tribromophenol were detected at 1.8 and 2.1 ng/g dry weight, respectively. At sampling station 13x, the two HPs were detected at 0.3 and 1.5 ng/g dry weight, respectively.

Data about concentrations of halophenols in marine sediments in areas exposed to chlorinated effluents are very scarce. In a previous study, Sim et al. (2009) investigated the occurrence and distribution of halogenated phenols in sediments obtained from a marine environment

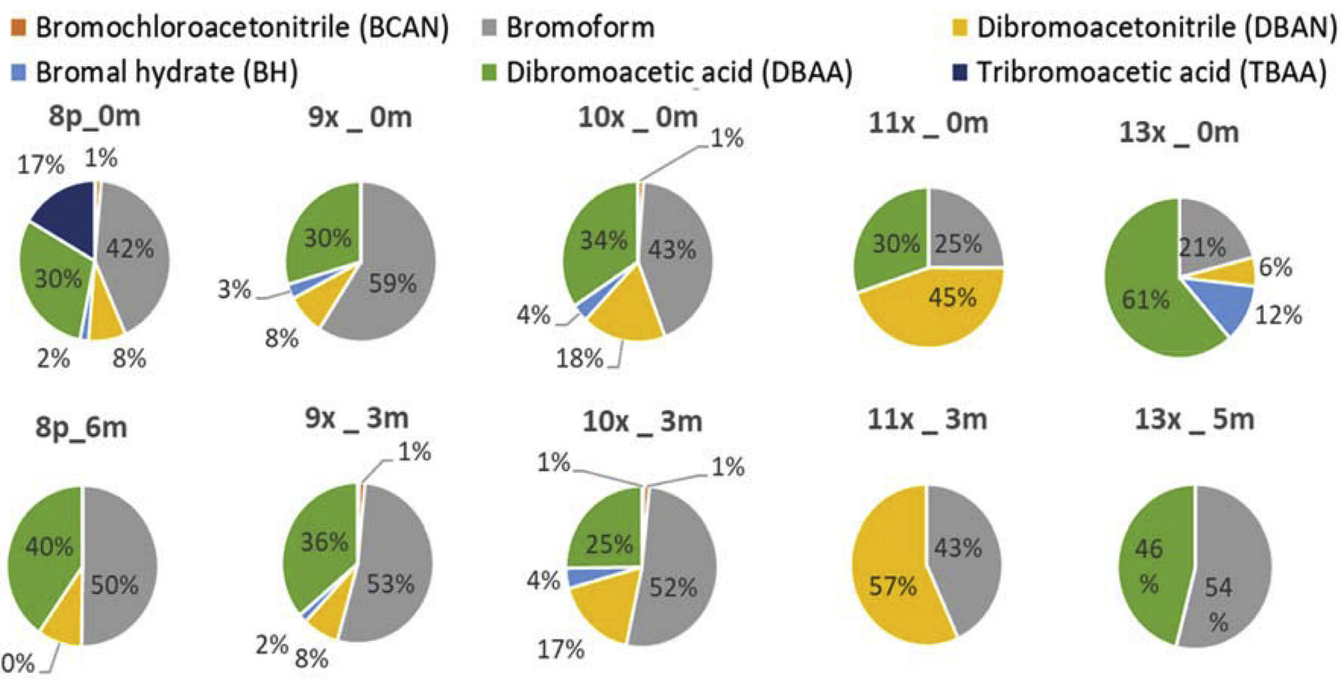

Fig. 6. Percentage distribution of the major CBPs in seawater near the chlorinated industrial outlets at the surface (upper figures) and at the bottom/depth (lower figures).

near a nuclear power plant in South Korea. According to the findings of the latter study, bromophenols were found at higher concentrations than chlorophenols. The reported mean concentration of 2,4,6-tribromophenol reached 3.78 ng/g dry weight in spring. Furthermore, 2,4,6-tribromophenol was previously detected at concentrations ranging from 2.80 to 10.39 µg/kg wet weight in the muscles of conger eel fish obtained from the Gulf of Fos (Boudjellaba et al., 2016). Based on the geographical distribution of contaminated conger eel fish near chlorination outlets in the latter study, authors suggested that the contamination of fish by 2,4,6-tribromophenol resulted – at least partially – from chlorination water discharges. In the present study, the sampling stations where contaminated sediments were detected, were not the ones located nearest to the chlorination outlets. Bromophenols can be produced from both natural and anthropogenic sources (WHO, 2005). Natural sources include marine organisms such as algae and benthic animals, while anthropogenic sources include chlorination of seawater and synthesis for use as intermediates in the production of flame retardants. In the analysis of HPs in seawater, all levels were below DL. However, very low levels below DL cannot be ruled out. With the effect of chronic presence, and a potential to sorb and accumulate in sediments, this would lead to detectable and quantifiable levels in sediments. Further investigations are necessary to discriminate whether the halophenols detected in sediments originate from the chlorination of seawater or are produced naturally. Nevertheless, the occurrence of 2,4,6-tribromophenol in the marine environment remains an issue of concern, since this compound has been reported to induce several significant adverse effects on fish populations (Deng et al., 2010).

4. Conclusions

This study measured the concentrations of CBPs in a semi-enclosed bay receiving industrial chlorinated seawater effluents. The highest levels of CBPs including bromoform, DBAA, DBAN, and BH were detected near industrial outlets. To our knowledge, BH was reported here for the first time in the context of industrial seawater chlorination. Other CBPs including TBAA and BCAN were detected at some sampling stations. At distant offshore sampling stations, only bromoform was detected at low levels. Furthermore, analysis of CBPs in sediments showed the presence of two HPs (2-chloro-4-bromophenol and 2,4,6-tribromophenol) which were not detected in seawater samples. Although CBPs at these low concentrations aren't expected to constitute a threat to human health via direct exposure, concerns regarding ecotoxicity and indirect human exposure (via seafood) need to be addressed. Despite low levels, a potential adverse effect to biota or accumulation in seafood (thus indirect human exposure) can't be ruled out, especially that CBPs are being discharged into water in a chronic manner. Therefore, to address these remaining concerns, suitable ecotoxicological assays of CBPs using adequate bioassays at environmentally relevant concentrations and risk assessment studies are warranted to assess the potential impact of the detected CBPs on environmental health. It's also recommended to conduct an extensive evaluation of contamination of marine organisms by CBPs in seawater exposed to chlorinated effluents in future studies.

Conflicts of interest

Authors declare no conflicts of interests.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijheh.2018.06.008.

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Supplementary Information

Occurrence and speciation of chlorination byproducts in marine waters and sediments of a semi-enclosed bay exposed to industrial chlorinated effluents

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Content

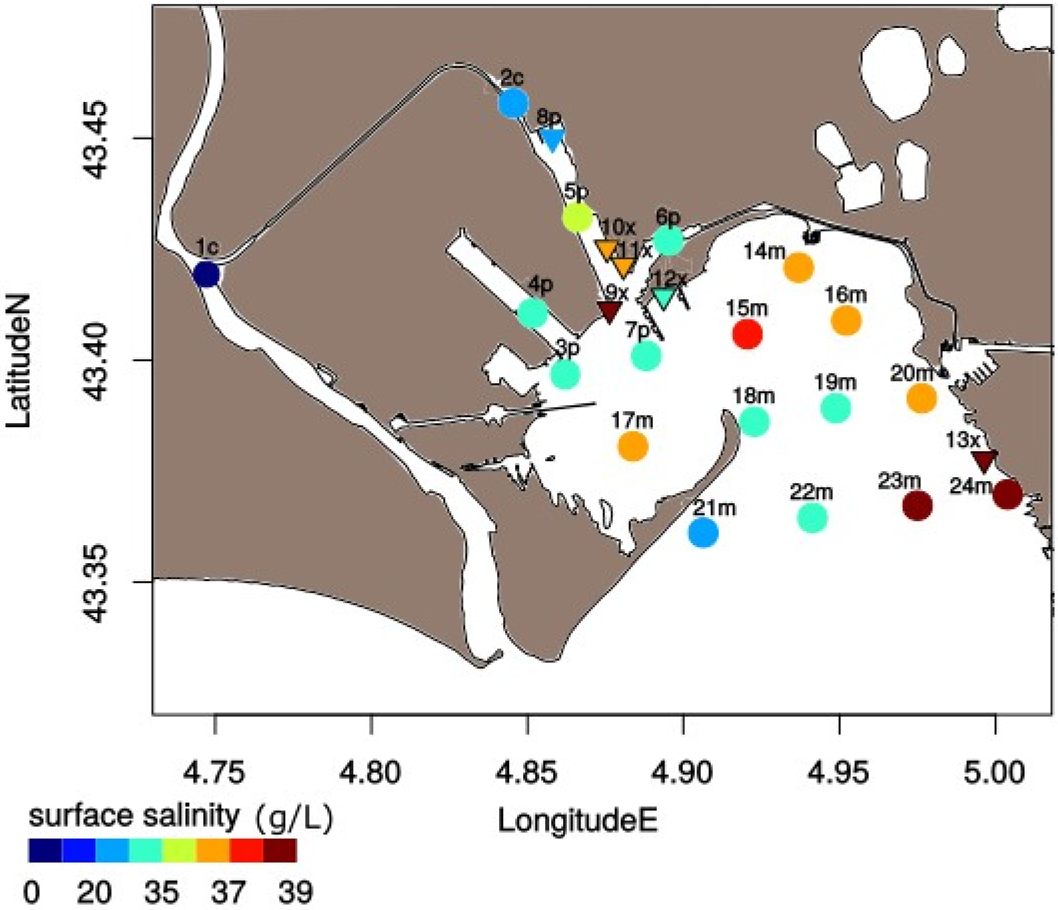

Figure S1. Variation of surface water salinity (in g/L) at the different sampling stations. Triangles represent industrial effluent discharge points.

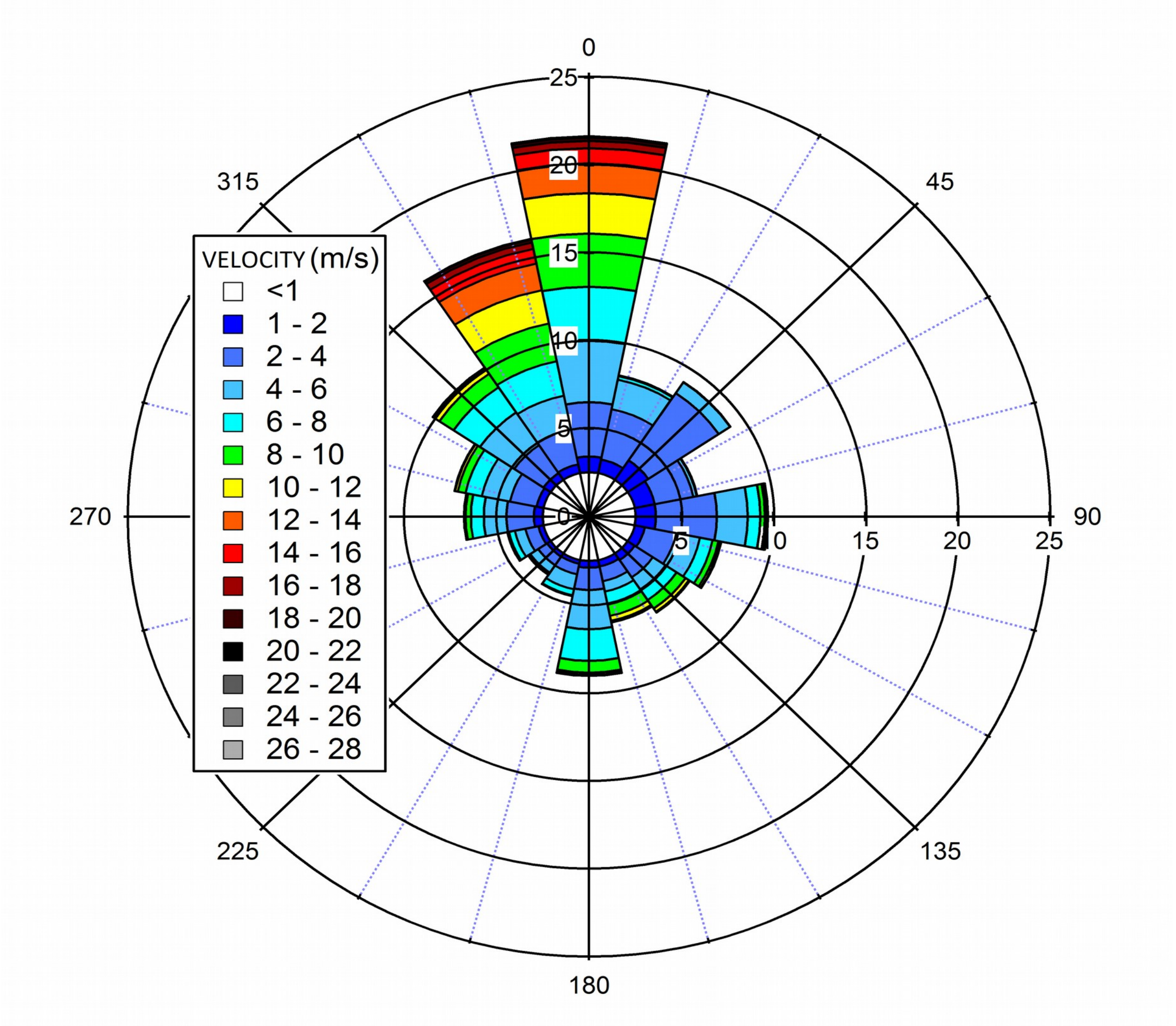

Figure S2. Wind rose for the region based on data from 2002 to 2011 (adapted from Météo France).

Method Detection Limits and Quantification Limits

The method detection limits (DLs) and quantification limits (QLs) for the analysis of CBPs and other parameters are listed in Table S1. DLs for each analyte were calculated by injecting 10 replicates of a fortified solution at a concentration estimated to be near the DL. DLs and QLs were estimated as 3 times and 10 times the signal-to-noise ratio, respectively

Table S1. Performance characteristics of the used analytical methods

Chemical (Unit)	**DL**	**QL**	**RSD (%)**	**Recovery (%)**	**Range**	**Linearity (r^2)**
			n=7, 0.1 µg/L			
Bromodichloromethane (µg/L)	0.01	0.05	3.9	130	0.03-1.00	0.998
Dibromochloromethane (µg/L)	0.01	0.03	4.1	93	0.03-1.00	0.999
Bromoform (µg/L)	0.01	0.04	4.5	99	0.02-1.00 1.00-20.00	0.997 0.991
			n=10, 0.1 µg/L			
Dichloroacetonitrile (DCAN) (µg/L)	0.007	0.02	2.7	93	0.02-2.00	0.998
Trichloroacetonitrile (TCAN) (µg/L)	0.04	0.16	11.2	87	0.10-1.00	0.993
Bromochloroacetonitrile (BCAN) (µg/L)	0.008	0.02	3.6	75	0.02-2.00	0.999
Dibromoacetonitrile (DBAN) (µg/L)	0.007	0.02	3.0	85	0.02-2.00	0.999
			n=8, 0.05 µg/L			
2-Bromo 4-chlorophenol (2B4CP) (µg/L)	0.008	0.02	6.0	95	0.01-1.00	0.999
2.6 Dibromophenol (2.6 DBP) (µg/L)	0.009	0.03	6.0	104	0.03-0.60	0.995
2.4 Dibromophenol (2.4 DBP) (µg/L)	0.006	0.02	4.0	107	0.02-1.00	0.999
2.4.6 Tribromophenol (2.4.6 TBP) (µg/L)	0.003	0.01	1.6	138	0.03-1.00	0.992
			n=8, 0.5 µg/L			
Monobromoacetic acid (MBAA) (µg/L)	0.9	2.7	15	84	3.0-10	0.991
Dichloroacetic acid (DCAA) (µg/L)	0.08	0.28	6.1	91	0.3-2.0	0.994
Trichloroacetic acid (TCAA) (µg/L)	0.12	0.43	9.2	92	0.3-2.0	0.996
Bromochloroacetic acid (BCAA) (µg/L)	0.11	0.38	6.8	111	0.3-5.0	0.999
Dibromoacetic acid (DBAA) (µg/L)	0.10	0.30	6.9	91	0.3-2.0	0.996
Bromodichloroacetic acid (BDCAA) (µg/L)	0.09	0.31	10.7	116	0.3-2.0	0.992
Chlorodibromoacetic acid (CDBAA) (µg/L)	0.12	0.44	6.9	128	0.5-5.0	0.994
Tribromoacetic acid (TBAA) (µg/L)	0.14	0.45	7.9	113	0.5-5.0	0.994
			n=7, 0.05 µg/L			
Bromal hydrate (BH) (µg/L)	0.01	0.0	5.3	149	0.03-1.00	0.999

		4				
			n=7, 0.1 mg/L			
Free Residual Chlorine (mg/L)	**0.03**	**0.1**	36	102	0.1-1.0	0.993
Total Chlorine (mg/L)	**0.03**	**0.1**	36	102	0.1-1.0	0.993
			n=7,1 mg/L			
Total Organic Carbon (TOC) (mg C/L)	0.11	0.33	2.4	144	0.3-3.0	0.990
			n=7, 1 mg/L			
Total Nitrogen (TN) (mg N/L)	0.17	0.51	9.7	270	0.2-2.0	0.990

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Table S2. Physicochemical parameters of water at the surface and the bottom (surface; bottom).

	Water Temperature (°C)	**pH**	**Salinity (g/L)**	**$[Br^-]$ (mg/L)**	**Free Oxidant (mg/L)**	**Total Oxidant (mg/L)**	**TOC (mg/L)**	**TN (mg/L)**
1c	15.9; 15.1	8.34; 8.08	2.2; 18.7	3.13; 3.10	<QL	<QL	2.16; 1.85	1.33; 1.08
2c	15.9; 15.8	8.09; 8.13	24.2; 34.2	39.72; 56.70	<QL	<QL	2.54; 1.5	0.8; <QL
3p	15.1; 14.9	8.22; 8.22	34.8; 36.5	51.43; 53.75	<QL	<QL	1.53; <QL	<QL
4p	15; 14.7	8.24; 8.21	34.9; 38.0	53.35; 58.73	<QL	<QL	1.26; 1.02	<QL
5p	15.3; 15.2	8.25; 8.24	35.2; 36.8	56.45; 59.23	<QL	<QL	1.24; 1.19	<QL
6p	15.4; 14.9	8.23; 8.25	34.5; 37.2	58.21; 64.68	<QL	<QL	1.72; 1.3	<QL
7p	15; 14.7	8.17; 8.12	34.0; 37.9	56.19; 69.34	<QL	<QL	1.99; 1.14	<QL
8p	15.7; 15.2	8.23; 8.25	29.1; 37.7	46.60; 54.17	<QL	<QL	3.02; 1.7	<QL
9x	18.9; 17.5	8.21; 8.22	38.0; 37.7	62.04; 66.93	<QL	<QL	1.87; 1.44	<QL
10x	17.9; 16.9	8.24; 8.24	36.6; 36.9	58.81; 61.12	<QL	<QL	2.18; 1.51	<QL
11x	17.1; 19.8	8.24; 8.22	36.2; 37.5	55.78; 63.11	<QL	<QL	1.92; 1.64	<QL
12x	15.5; 13.7	8.28; 8.28	33.1; 34.2	66.33; 62.11	<QL	<QL	1.33; 1.37	<QL
13x	16.5; 14.3	8.2; 8.24	38.4; 38.7	58.60; 59.21	<QL	<QL	2.01; 2.08	<QL
14m	15; 14.4	8.24; 8.22	36.8; 38.5	53.79; 59.59	<QL	<QL	1.47; 1.69	<QL
15m	15; 14.2	8.24; 8.23	37.3; 38.4	54.86; 57.09	<QL	<QL	1.84; 1.45	<QL
16m	14.9; 14.3	8.25; 8.22	36.5; 38.5	52.82; 56.30	<QL	<QL	1.44; 1.58	<QL
17m	14.9; 14.3	8.21; 8.18	36.2; 38.1	56.20; 56.49	<QL	<QL	1.99; 1.38	<QL
18m	15.2; 14	8.23; 8.23	33.6; 38.6	46.69; 59.57	<QL	<QL	1.86; 1.3	<QL

19m	14.8; 14.3	8.24; 8.23	33.2; 38.5	43.09; 56.50	<QL	<QL	1.72; 1.58	<QL
20m	15.1; 14.4	8.23; 8.21	36.3; 38.6	52.26; 57.92	<QL	<QL	1.47; 2.08	<QL
21m	14.1; 14.2	8.17; 8.13	29.8; 38.2	44.19; 58.17	<QL	<QL	2.13; 1.32	0.55; <QL
22m	14.2; 14.2	8.22; 8.21	33.6; 38.4	51.29; 58.69	<QL	<QL	2.17; 1.54	<QL
23m	14.6; 14.3	8.22; 8.23	38.3; 38.3	57.50; 58.54	<QL	<QL	1.83; 1.48	<QL
24m	14.5; 14.6	8.22; 8.24	38.6; 38.7	57.72; 57.52	<QL	<QL	1.47; 1.26	<QL

Table S3. Concentrations (in µg/L) of chlorination byproducts (CBPs) in seawater at the surface and the bottom (surface; bottom). Concentrations below DL are represented by hyphens.

	Bromoform	**DBAA**	**DBAN**	**BCAN**	**BH**	**TBAA**
1c	- ; -	- ; -	- ; -	- ; -	- ; -	- ; -
2c	0.27; 0.55	- ; 0.43	0.07; 0.11	- ; -	- ; -	- ; -
3p	0.05; 0.08	- ; -	- ; -	- ; -	- ; -	- ; -
4p	0.05; 0.15	- ; -	- ; 0.05	- ; -	- ; -	- ; -
5p	0.47; 0.77	0.56; 0.44	0.10; 0.12	- ; -	- ; -	- ; -
6p	0.24; 0.34	0.35; -	0.07; 0.08	- ; -	- ; -	- ; -
7p	<QL ; 0.31	- ; -	- ; 0.08	- ; -	- ; -	- ; -
8p	**1.95; 0.68**	**1.40; 0.54**	**0.36; 0.12**	**0.05; -**	**0.08; -**	**0.77; -**
9x	**1.49; 1.81**	**0.74; 1.24**	**0.20; 0.26**	**- ; 0.04**	**0.07; 0.06**	**- ; -**
10x	**1.62; 2.36**	**1.29; 1.15**	**0.67; 0.79**	**0.04; 0.05**	**0.13; 0.18**	**- ; -**
11x	**0.30; 0.41**	**0.36; -**	**0.53; 0.54**	**- ; -**	**- ; -**	**- ; -**
12x	**<QL ; <QL**	**- ; -**	**- ; -**	**- ; -**	**- ; -**	**- ; -**
13x	**0.17; 0.46**	**0.52; 0.39**	**0.05; -**	**- ; -**	**0.10; -**	**- ; -**
14m	0.09; 0.11	- ; -	- ; -	- ; -	- ; -	- ; -
15m	0.19; 0.16	- ; -	- ; -	- ; -	- ; -	- ; -
16m	0.06; 0.16	- ; -	- ; -	- ; -	- ; -	- ; -
17m	0.12; 0.16	- ; -	- ; -	- ; -	- ; -	- ; -
18m	<QL ; <QL	0.44; -	- ; -	- ; -	- ; -	- ; -

19 m	<QL ; 0.06	- ; -	- ; -	- ; -	- ; -	- ; -
20 m	0.07; 0.04	- ; -	- ; -	- ; -	- ; -	- ; -
21 m	<QL ; <QL	- ; -	- ; -	- ; -	- ; -	- ; -
22 m	- ; <QL	- ; -	- ; -	- ; -	- ; -	- ; -
23 m	<QL ; <QL	- ; -	- ; -	- ; -	- ; -	- ; -
24 m	0.57; 0.64	0.42; 0.45	- ; -	- ; -	- ; -	- ; -

BCAN: bromochloroacetonitrile; DBAN: dibromoacetonitrile; BH: bromal hydrate; DBAA: dibromoacetic acid ; TBAA: tribromoacetic acid.

Dibromochloromethane was detected at some sampling stations (8p, 9x, 10x) at levels lower than QL. Halophenols were not detected in water.

Table S4. Depth of collected sediments

Sediment Sample	**Depth (m)**
8p	7.4
11	6.5
12x	4.7
13x	8
14m	7.18
15m	11.5
17m	5.1
19m	24.5
22m	17.8
24m	6.2