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Tarek Manasfi, Karine Lebaron, Maxime Verlande, Julien Dron, Carine Demelas, et al.. Occurrence and speciation of chlorination byproducts in marine waters and sediments of a semi-enclosed bay exposed to industrial chlorinated effluents. *International Journal of Hygiene and Environmental Health*, 2019, 222 (1), pp.1-8. 10.1016/j.ijheh.2018.06.008 . hal-01845452

HAL Id: hal-01845452

<https://amu.hal.science/hal-01845452>

Submitted on 31 Jul 2018

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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.

Keywords

Chlorination byproducts; Disinfection byproducts; Industrial chlorinated effluents; Cooling water; Marine sediments; Seawater pollution

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 can result from the growth of microorganisms on surfaces where they form biofilms or the growth of macro-organisms such as clams. Biofilms tend to stick to heat-exchange surfaces, thereby significantly reducing heat-transfer coefficients. In some cases, excessive biofouling can lead to plugging of heat exchangers. There are several techniques for preventing biofouling of both types. The use of chlorine to avoid biofouling is among the most common procedures (Khalanski

and Jenner, 2012). Chlorine is added 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, 1999b; Ma et al., 2011; Khalanski and Jenner, 2012). When chlorine is added to seawater, it reacts with organic and inorganic compounds present in seawater leading to the formation of a range of chlorination byproducts (CBPs) (Boudjellaba et al., 2016). Factors such as the initial chlorine dose, temperature, pH, constitution of seawater and ultimately presence of contaminants (natural or anthropogenic) can influence these reactions leading to significant differences in the nature and levels of the different formed CBPs (Allonier et al., 1999). The release of CBPs into the environment constitutes a concern from environmental and health standpoints. Even if the levels of CBPs formed in seawater tend to be low, their effects on the long term cannot be neglected since they are usually contained in large volumes of water over extended geographical area and for prolonged periods of time (Boudjellaba et al., 2016). In this way, chlorine itself and its byproducts can constitute a threat to marine ecosystems (Taylor, 2006; Deng et al., 2010; Pignata et al., 2012; Khalanski and Jenner, 2012). Furthermore, the spectrum of possible adverse risks is not limited to the environment since potential volatilization and subsequent photolysis of CBPs into reactive species in the atmosphere may affect human health upon exposure to CBPs or their products (Quack and Wallace, 2003; Parinet et al., 2012). Most of studies conducted previously on CBPs in the marine environment focused on nuclear and thermal power plants (Allonier et al., 1999; Khalanski and Jenner, 2012). These investigations looked into a limited number of compounds in cooling water effluents, often at a single or a few discharge points in the open coast. To date, data about the contamination of seawater and marine sediments exposed to multiple industrial chlorinated effluents remain very scarce. The

present study investigated the contamination of seawater and sediments by CBPs in the Gulf of Fos, Southeastern France. 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 Rhône river, among other freshwater inputs (Ulses et al., 2005). The Gulf of Fos hosts the largest port of trade in France and in the Mediterranean Sea (Marseille-Fos Port) along with a major industrial zone that includes steel, petrochemical, waste incineration, and cement industries as well as gas and electricity power plants. The aim of the study was to characterize the contamination of the bay by halogenated CBPs. For this reason, 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), and chlorine levels were also determined. Data provided by this study are crucial for any future risk assessment study for the marine pollution in the Gulf of Fos or similar marine environments.

Materials and Methods

Study Site

The study investigated the Gulf of Fos (Figure 1) located in Southeastern France, on the Mediterranean, and at about 50 km from the city of Marseille. Average water depth in the Gulf is of about 20 m. The Gulf of Fos is a semi-enclosed bay which receives several freshwater inputs with the main input being from the Rhône River. Other minor inputs include the Berre Lagoon, irrigation and navigation canals. The

region is characterized by frequent and strong north winds (around 40% per year) and southeast winds (10 to 20% per year).

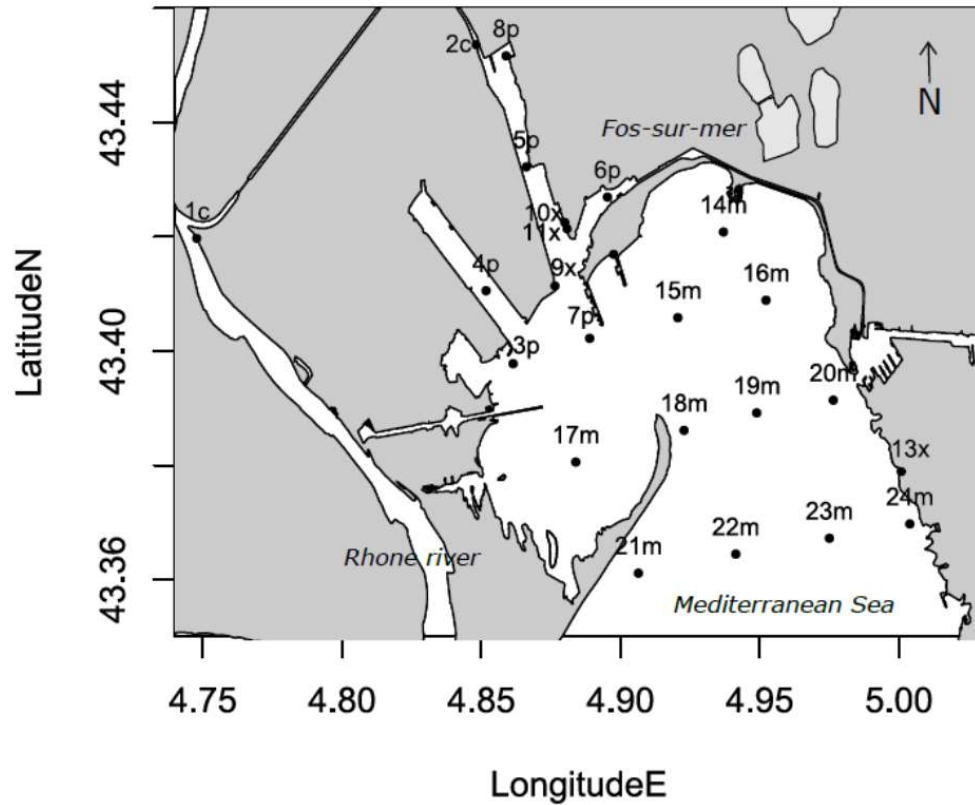


Fig. 1. Overview of the Gulf of Fos and the different sampling stations (from 1c to 24m).

Fos is the host of the largest industrial zone in southern Europe. Various heavy industrial activities are established around the Gulf including two large liquefied natural gas (LNG) terminals (Fos-Cavaou and Fos-Tonkin, which are designated by sampling stations 12x and 8p, respectively). These two LNG terminals, Fos-Cavaou and Fos-Tonkin, discharge chlorinated waters at a flow of 30,000 m³/h and 15,000 m³/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 10x) which discharge chlorinated water (by electrochlorination). Metal industry (sampling station 11x) and oil refineries (sampling station 13x) also discharge chlorinated seawater at flows exceeding 10,000 m³/h.

Sample Collection

Sampling campaign was performed during spring (24, 25, and 26 April 2017). When sampling was performed, sustained southeast wind (35-40 km/h on average according to MétéoFrance, Istres) with gusts. The different sampling stations were located within the Gulf of Fos and included the main industrial outlets (sampling station names end with x) (Figure 1). Water samples were collected at all the 24 sampling stations. At each sampling station, seawater samples were collected at the surface (depth between 0 to 50 cm) and at 7m depth (or the bottom at the stations where the bottom is at depth < 7 m). Seawater samples were collected using a 5-L Niskin bottle (General Oceanics, USA). For the analysis of CBPs, sample aliquots (1 L) were placed in amber glass bottles with PTFE-lined screw caps and ascorbic acid was rapidly added to these bottles to quench any residual free chlorine. 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).

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

Chemicals

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 ASTM International standard practice for the preparation of substitute ocean water (method D1141-98, 2013).

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. For the different

chemical classes, specific internal standards were added. For THMs, HANs and BH, the internal standard 1,2,3-trichloropropane was used according to U.S.EPA 551.1 (Munch and Hautman, 1995). Samples were then 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 (Domino et al., 2003) was used with slight modifications. In brief, sample aliquots (40 mL) were acidified to a $\text{pH} < 1$ 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. (1999) with some modifications. In brief, 50 mL samples were mixed manually during 4 minutes 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.

Analytical methods

Free residual chlorine and total chlorine 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). The pre-treated sample was injected (50 µl) into the furnace filled with a Pt preconditioned catalyst. The combustion was realized at 800 °C and the combustion products were carried by high purity oxygen (Linde Gas) allowing detection of CO₂ 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 ⁶³Ni 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 10 ng/L to 10 µg/L. 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 and later conducting the same treatment as that of samples. Seawater and purified water reagent blanks were included with each sequence. Analysis of samples was conducted in duplicate. The detection limits (DL) and the quantification limits (QL) for the analyzed chemicals and parameters and their estimation procedure are presented in supplementary information (Table S1).

Maps were produced using the software: R (R Core Team, 2015) and Inkscape (Inkscape, 2015).

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, 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.

Results and Discussion

Physicochemical parameters

At the different sampling stations, physicochemical parameters including water temperature, pH, salinity, TOC, TN, bromide content, and levels of free residual chlorine, and total chlorine were determined. Table S2 presents the measurements of the physicochemical parameters at the sampling stations. Very little variation was observed in the pH among the different sampling points located throughout the gulf

(pH ranged between 8.13 to 8.25). Salinity varied among the different sampling stations especially at the surface (Figure 2). A marked influence of the Rhone River freshwater intrusion appeared at stations located nearby (2c, 8p and 5p) which had lower salinities than the sampling stations located offshore.

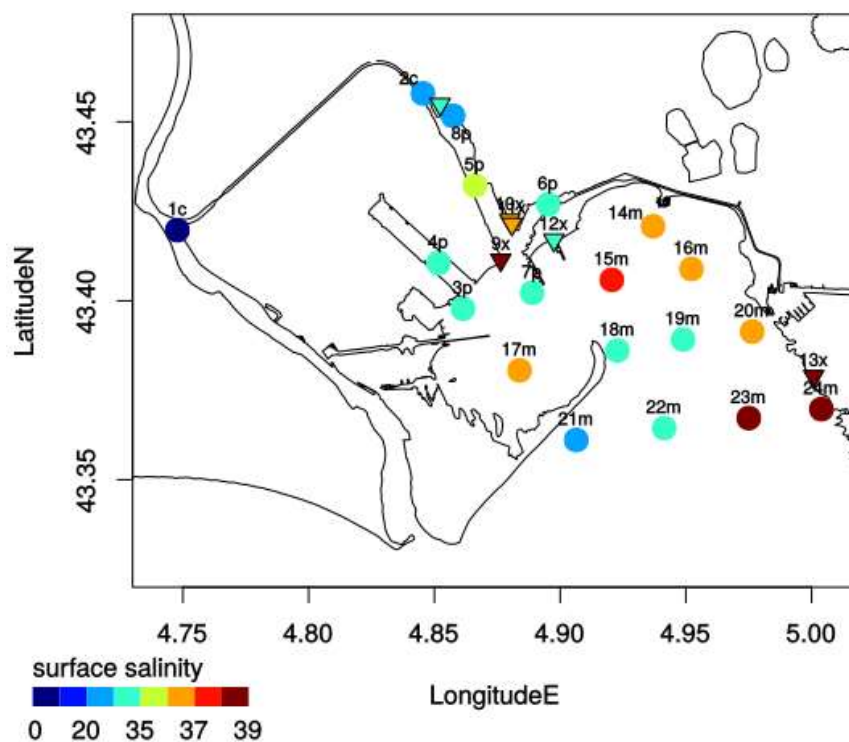


Figure 2. Variation of surface water salinity (in g/L) at the different sampling stations

The southeastern wind seems to drive these less salty waters to the western part of the Gulf as appeared at the surface at stations 17m, 18m, 19m, 21m and 22m. At the bottom (or at 7 m depth) the salinity was generally homogeneous (> 37 g/L), but remained slightly lower in the eastern sector. The sampling station 2c, which was 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 is probably resulting from the vigorous mixing of the Rhône River freshwater with seawater coming from the Gulf of Fos especially that on the day of sampling moderate to strong southeast winds were registered. Bromide concentrations were generally

homogenous among the different sampling stations within the Gulf (Table S2). Bromide levels were relatively high even at points close to the intrusion of freshwater of the Rhone River. Bromide levels at sampling stations 3p to 8p ranged from 46.6 to 58.21 at the surface, and from 53.75 to 69.34 at the bottom/depth. Temperature at the surface and in deep water are presented in Table S2. Excluding outlets, water temperatures at the bottom were globally homogeneous across the Gulf. Water temperature was 14.5 to 15 °C at the surface and 14 °C at the bottom/depth. This very little gradient is compatible with the agitated conditions that favor the mixing of water bodies. The temperature of freshwater (1c, 2c) was slightly higher (15 to 16 °C). Near the outlets at sampling stations 9x, 10x, 11x, temperatures were slightly higher at the surface (up to 18.9 °C) and the bottom (up to 19.8 °C), due to the discharge of heated seawater from the nearby industries. In general, the surface temperatures at the sampling stations close to the shore were higher than offshore stations (Figure 3).

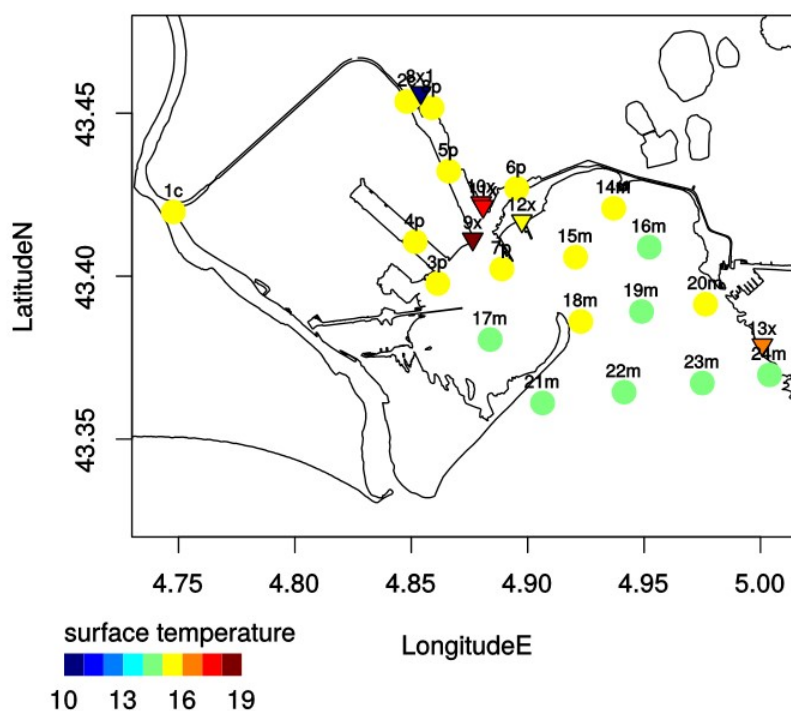
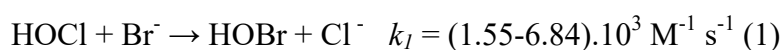


Figure 3. Variation of surface water temperature (in °C) at the different sampling stations

Occurrence of chlorination byproducts (CBPs) in seawater

The levels of the CBPs identified in the Gulf of Fos are presented in Table S3. Several CBPs belonging to different chemical classes were detected in the Gulf. The main detected CBPs included 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). Chloroform was detected at some sampling stations at levels below the QL. The occurrence of predominantly brominated CBPs in chlorinated seawater can be explained by the formation of bromine upon the addition of chlorine to seawater. This speciation is in agreement with previous studies that reported the formation of brominated byproducts in chlorinated bromide-containing water (Ged and Boyer, 2014). 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):



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., 2017). Bromine species such as Br₂, Br₂O, BrOCl, and BrCl are less abundant but more reactive than HOBr and OBr⁻ and have been shown to contribute to bromination of some organic compounds (Sivey et al., 2013). Table 1 shows the equilibrium concentrations of bromine species when seawater containing 67 mg/L bromide, at pH 8.05, is chlorinated with active chlorine (2 mg/L). These concentrations were estimated using PHREEQC (Parkhurst and Appelo, 2013).

Table 1. Molar concentrations of bromine species at equilibrium in seawater (Bromide 67 mg/L; 20 g/L chloride at pH 8.05; chlorinated with 2 mg/L active chlorine), calculated using PHREEQC.]

Bromine Species	Concentration (M)
HOBr	3.85 x 10 ⁻⁵
OBr ⁻	1.67 x 10 ⁻⁵
Br ₂	2.73 x 10 ⁻⁸
Br ₂ Cl ⁻	1.83 x 10 ⁻⁸
Br ₂ O	1.08 x 10 ⁻⁸
BrCl	7.61 x 10 ⁻¹⁰
Br ₃ ⁻	3.29 x 10 ⁻¹⁰
BrCl ₂ ⁻	2.55 x 10 ⁻¹⁰
BrOCl	2.44 x 10 ⁻¹²

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). At these outlets, the concentration of bromoform ranged from 0.17 to 1.95 µg/L (at the surface) and from 0.46 to 2.36 µg/L (at the bottom). At the sampling station 12x (in the vicinity of the outlet of LNG Fos-Cavaou terminal), surprisingly low concentrations were detected. This aberration is probably due to the dislocation of the sampling Niskin bottle under the effect of wind during sampling. At its exit at sea, station 12x, at 150 m from the shore, strong wind and current of south-east, made the measurements and sampling very difficult. Throughout the studied area of the Gulf, bromoform concentrations ranged from 0.05 to 1.95 µg/L and from 0.06 to 2.3 µg/L at the surface and the bottom, respectively. 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 slightly higher temperatures. For the other CBPs, distinctive discrepancies between bottom and surface levels were not observed. DBAA concentrations ranged from 0.35 to 1.40 $\mu\text{g/L}$ and from 0.39 to 1.23 $\mu\text{g/L}$ at the surface and the bottom, respectively. DBAN concentrations ranged from 0.049 to 0.67 $\mu\text{g/L}$ and from 0.05 to 0.79 $\mu\text{g/L}$ at the surface and the bottom, respectively. BCAN was detected at concentrations ranging from 0.04 to 0.05 $\mu\text{g/L}$ at the surface and the bottom. BH concentrations ranged from 0.075 to 0.13 $\mu\text{g/L}$ and from 0.06 to 0.18 $\mu\text{g/L}$ at the surface and the bottom, respectively. Overall, the concentrations of CBPs detected in the Gulf of Fos in the present study were relatively low compared to levels previously reported for these compounds in seawater exposed to industrial chlorinated effluents. In a survey conducted in coastal power stations, at the point of discharge, bromoform concentrations varied from 3.1 $\mu\text{g/L}$ to 29.20 $\mu\text{g/L}$ and DBAN concentrations varied from 0.10 $\mu\text{g/L}$ to 11.39 $\mu\text{g/L}$ (Khalanski and Jenner, 2012). Since many of the CBPs are volatile, increased volatilization with accentuated winds could be one reason. Another reason could be related to decrease in chlorination activity at some of the plants since water temperature were not very high which naturally decreases biofouling.

Despite the low concentrations, bromoform was still detected in the Gulf of Fos even at sampling stations that were relatively distant from the outlets (such as 14m, 15m, 16m, 17m, 19m, 20m, and 24m). The concentrations of bromoform at these sampling stations away from the outlets ranged from 0.06 to 0.57 $\mu\text{g/L}$ and from 0.06 to 0.64 $\mu\text{g/L}$ at the surface and the bottom respectively. These concentrations are superior to the typical background levels of bromoform emitted by marine algae in seawater that is not exposed to chlorinated effluents. The latter has been estimated at 0.025 $\mu\text{g/L}$,

and rarely exceed 0.1 $\mu\text{g/L}$ unless when extensive beds of macro-algae are present, which is not the case in the Gulf of Fos (Quack and Wallace, 2003). The diffusion of bromoform across the Gulf of Fos is represented in Figure 4. This figure shows that shows contamination of the Gulf of Fos with bromoform at concentrations lower than what is detected near the outlets, yet higher than what is found in uncontaminated seawater.

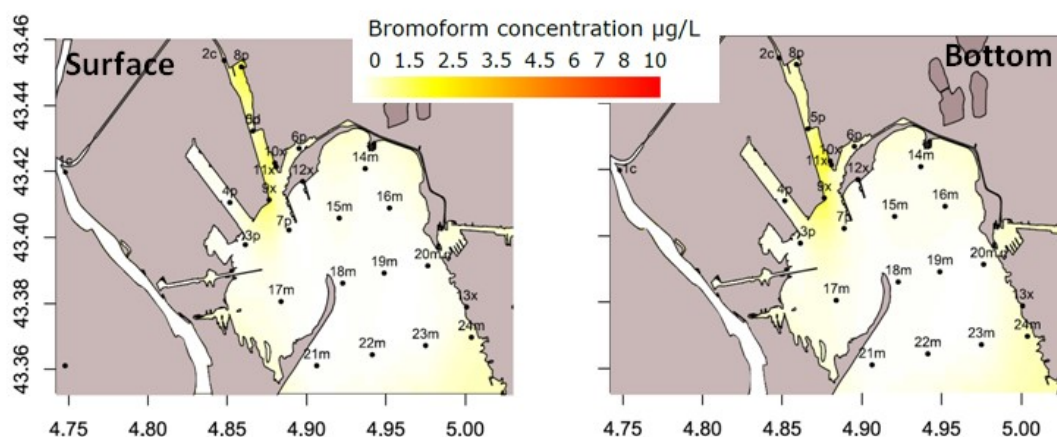


Figure 4. Diffusion of bromoform in seawater across the Gulf of Fos at the surface (left figure) and at the bottom/depth (right figure).

Distribution of CBPs in seawater

Among the detected CBPs, bromoform was the most abundant species at most of the sampling stations (Figure 5).

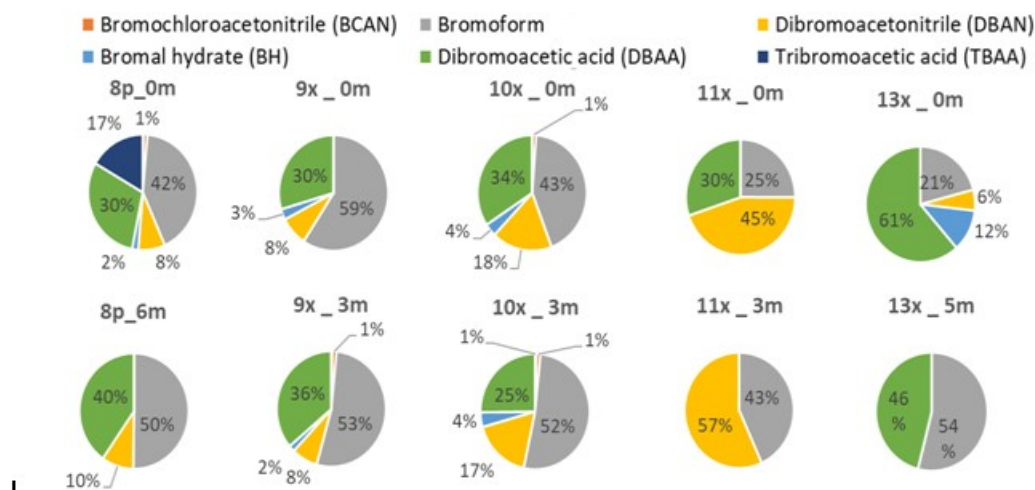


Figure 5. Percentage distribution of the major CBPs in seawater near the chlorinated industrial outlets at the surface (upper figures) and at the bottom/depth (lower figures)

This finding is in agreement with previous studies that investigated the occurrence of CBPs in seawaters exposed to chlorinated industrial effluents (Allonier et al., 1999; Boudjellaba et al., 2016; Jenner et al., 1997).

Another THM, dibromochloromethane was detected at levels below its QL. 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 high levels of nitrogen-containing organic compounds near the industrial outlet 11x. Furthermore, pH is another factor that has been shown to affect the speciation of CBPs (Cimetiere et al., 2010). Hansen et al. (2012) demonstrated that with decreasing pH, THM formation was reduced while HAN formation increased and HAA formation remained constant. However, in this study the influence of pH on the distribution of CBPs can be ruled out since the pH was largely homogenous across the Gulf (pH = 8.1 – 8.2). While DBAA was generally the second most abundant CBP, 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 (Manasfi et al., 2016; Zhang and Minear, 2002). It has been

reported that TBAA may decompose to form bromoform in aqueous solutions (Zhang and Minear, 2002). HPs were not detected in seawater samples.

Occurrence of brominated halophenols in sediments

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 level (of 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 (of dry weight). At sampling station 13x, the two HPs were detected at 0.3 and 1.5 ng/g (dry weight), respectively. To our knowledge, this is the first study to report the levels of some halophenols in marine sediments obtained from the vicinity of industrial chlorinated effluents. Although the detected HPs were brominated and therefore compatible with the general speciation of CBPs determined in seawater in the Gulf, further investigations are necessary to discriminate whether the detected halophenols originate from the chlorination of seawater or are produced from algal species and biota.

Conclusions

Seawater in the Gulf of Fos which is exposed to multiple industrial chlorinated effluents contained predominantly the brominated CBPs bromoform, DBAA, DBAN, and BH. Other CBPs including TBAA and BCAN were also detected at some sampling stations. The levels of CBPs were relatively low compared to levels reported in the literature for seawater exposed to chlorinated effluents from nuclear plants and other industries which employ chlorination. Despite the low levels, bromoform was found at sampling stations relatively far from the chlorinated effluent outlets at concentrations superior to what is found naturally in uncontaminated seawater. In

sediments, two HPs namely 2-chloro-4-bromophenol and 2,4,6-tribromophenol were detected at two sampling stations. Since the concentrations of CBPs depend on many factors including meteorological conditions, season, and chlorination operations in the nearby industrial plants, future investigations that assess the levels of CBPs under different meteorological conditions and season are warranted. Furthermore, the importance of risk assessment studies that estimate the impact of the detected concentrations of CBPs on the environment is highlighted.

Conflicts of interest

Authors declare no conflicts of interests.

Acknowledgements

This work was funded by the French National Research Agency(ANR) within the project FOSSEA (ANR-16-CE34-0009). Authors acknowledge Météo-France for meteorological data through the agreement N° DIRSE/REC/16/02/0 and reviewers for helpful comments.

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