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Disinfection By-Products (DBPs) in Seawaters, Sediments and Biota near a Marine Terminal for Regasifying Liquefied Natural Gas (LNG) in the Northern Adriatic Sea (Italy)

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Abstract: In 2009, the first Italian offshore LNG terminal, located approximately 12 km from the coast of Italy in the Northern Adriatic Sea, started its operation phase. Even if the active chlorine concentration in the discharged seawater is within limits set by Italian regulations (0.2 mg/L), to verify the environmental impact of disinfection by-products (DBPs) on the ecosystem, a specific monitoring program was scheduled from 2010 to 2015. The present study is the first displaying results of DBPs in marine waters of the Adriatic Sea. During the first two years of monitoring activities, DBPs were slightly above limit of quantifications (LOQs) in all investigated matrices and limited to the nearest area around the terminal. In these surveys, bromoform was the most frequently detected compound in seawaters, while haloacetic acid presence, as well as transplanted mussels and fish fauna, mostly characterized sediments. In the following surveys, levels were mostly negligible in all matrices investigated, with values mostly below the specific LOQs of the different compounds.

Keywords: VDbPs; HAAs; HAPhs; biomonitoring; mussel watch; marine LNG terminal

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1. Introduction

The regasification liquefied natural gas (LNG) terminals play a strategic role for supplying gas [1]. During the regasification process seawater is used, and usually, to prevent growing of encrusting organisms on the circuits, withdrawn seawater is treated with sodium hypochlorite as antifouling agent.

The use of chlorine for the chlorination of water is one of the anthropogenic sources of some halo-compounds in seawater [2], since chlorine residues could give rise to chlorinated disinfection by-products (DBPs), which are chlorinated organic substances dangerous for ecosystems. In this context, among chlorinated DBPs, the predominant are volatile disinfection byproducts (VDbPs), haloacetic acids (HAAs), and halophenols (HAPhs). Indeed, a specific evaluation of these compounds is an essential part of the monitoring plan of LNG terminals.

In the seawater lifetimes of DBPs are dependent on temperature and biodegradation, and the detection of certain compounds may indicate the proximity to a source, as some compounds have very short lifetimes in both water and the atmosphere [3]. However, there are different sources of halo-compounds in seawater, both anthropogenic and natural [3].

Sediments can accumulate chemicals such as DBPs, but also play an important role in the adsorption and conversion of complex organic molecules into volatile organic compounds (VOCs) [3]. Moreover, they are not typically referred to as a natural source of VOCs [4].

Marine biota can produce halogenation, with bromide, rather than chlorine, as the most prevalent halogen found and produced in several organisms [5,6]. Very recently, mussels were used as bioindicators in ballast water discharged at several ports in the Adriatic Sea showing very low bioaccumulation levels for DBPs, despite their relatively higher concentration found in seawaters [7]. Bioaccumulation data for DBPs in fishes are still lacking.

In 2009, the first Italian offshore LNG terminal, located approximately 12 km from the coast of Italy in the Northern Adriatic Sea, started its operation phase [1,8]. Even if the active chlorine concentration in the discharged seawaters is within limits set by Italian regulations (0.2 mg/L), to verify the environmental presence of DBPs on the ecosystem, a specific monitoring program was scheduled from 2010 to 2015. Besides that, a multidisciplinary monitoring plan was also designed and implemented, to verify the possible impact on marine environment associated with the whole project [1,8–10].

Results of the present study aimed at reporting levels of DBPs detected during monitoring activities of the first LNG terminal in the Northern Adriatic Sea and describing the fate of detected compounds, in the marine environment, by comparing seawater and sediment concentrations with bioaccumulation levels in mussels and fish fauna.

The present study is the first displaying results of DBPs in marine waters in the Adriatic Sea.

2. Materials and Methods

The study area is located in the Northern Adriatic Sea, 12 km from the Italian coast (Figure 1). The water outfall of the regasification process is located in the south part of the terminal [8].

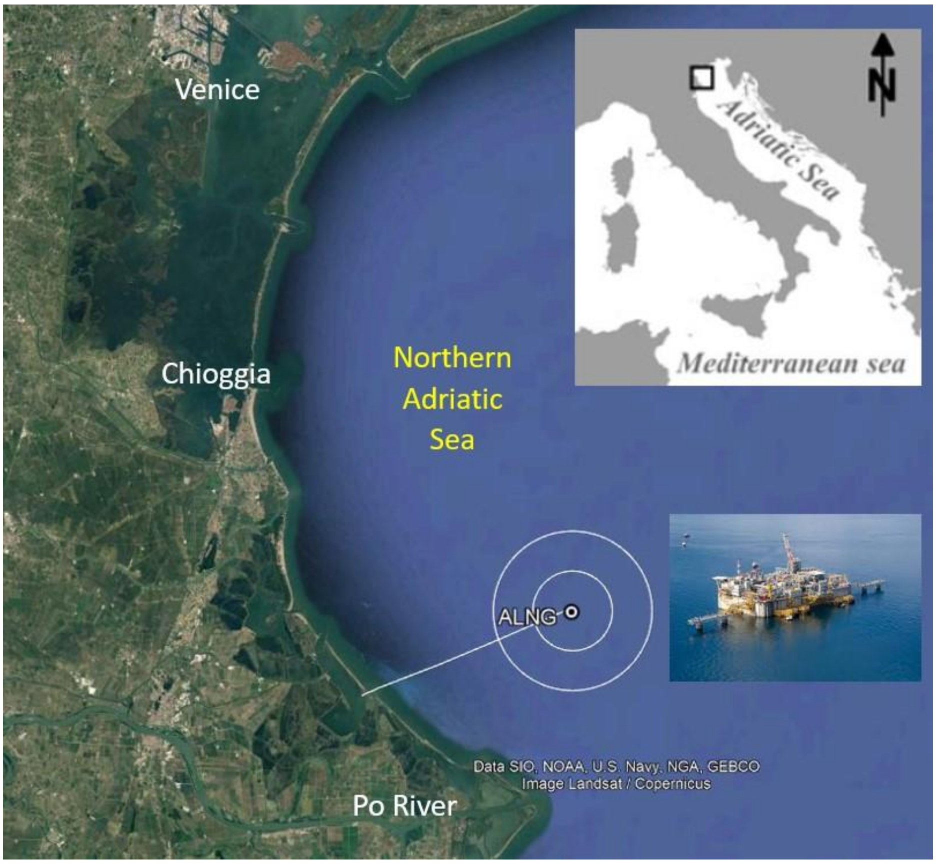

Figure 1. Study area and location of LNG terminal (ALNG) in the Northern Adriatic Sea. The terminal (see small photo) is enclosed by a "no entry zone" (1.5 nautical miles (nm) radius) and a "respect zone" (3 nm radius). The gas pipeline, connecting the ALNG to land, is also shown.

2.1. Sampling Strategy

The strategy for seawater and sediment sampling was based on distance from the terminal, with sites located along the principal cardinal axes. Sampling frequency for these matrices was annual.

Seawaters were sampled by ISPRA research vessel, by means of Niskin bottles (5 L), once a year from 2010 to 2015, from late spring to late summer, at 23 sites placed at 10, 20, 50, 75, 100, 150, 250, 500, and 1000 m from the terminal (Figure 2) along six cardinal axes: N, E, SE, S, SW, and W. Three sites, placed at 2000, 5000, and 10,000 m southward, were considered as controls. Three depth levels were collected for each site: surface, intermediate, and 1 m above sea bottom.

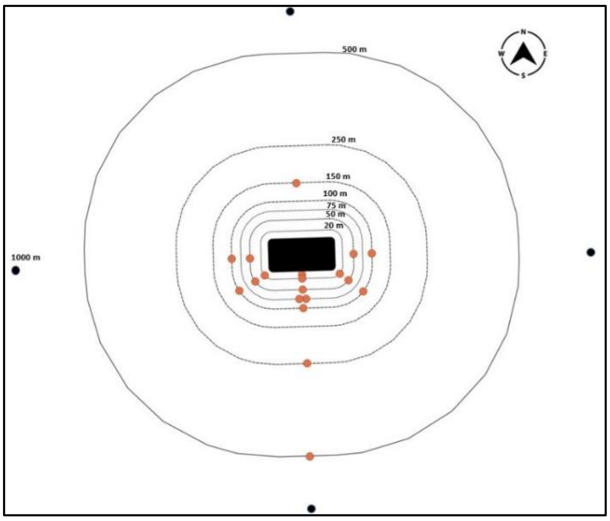

Figure 2. Seawater sampling sites monitored from 2010 to 2015 at several distances from the LNG terminal. Sampling sites at 1000 m (black dots) are not in scale.

During the yearly surveys with ISPRA research vessel, sediment samples were collected by means of a box-corer at 21 stations: 18 around the terminal (Figure 3) placed at 100, 200, 350, 500, 1000 m, and three at a control site 4000 m northwest (not showed in Figure 3). The top 5 cm were used for DBPs analysis.

Mussels (*Mytilus galloprovincialis*) were sampled by commercial and research vessels. Transplanted mussels (5 kg per site), coming from controlled mussel farms (T0), were placed at two sites, the first being at 10,000 m (as a control) and the latter at 500 m south of the terminal. In 2014 and 2015 surveys, mussels were transplanted also at 800 m south. At each site, a suspension system held the mussels at a few meters depth, and specimens were rescued every 4 weeks (T1). Transplanting frequency was higher during the first year (2011, four times between late spring and late autumn) and then twice a year (2012–2015, fall–winter or spring–summer).

Two sites were identified for fish fauna (commercial species) monitoring activities, on the basis of sidescan sonar surveys that revealed the presence of small to medium rocky outcrops on the bottom, 300 m north and 3 km southwest from the terminal (control).

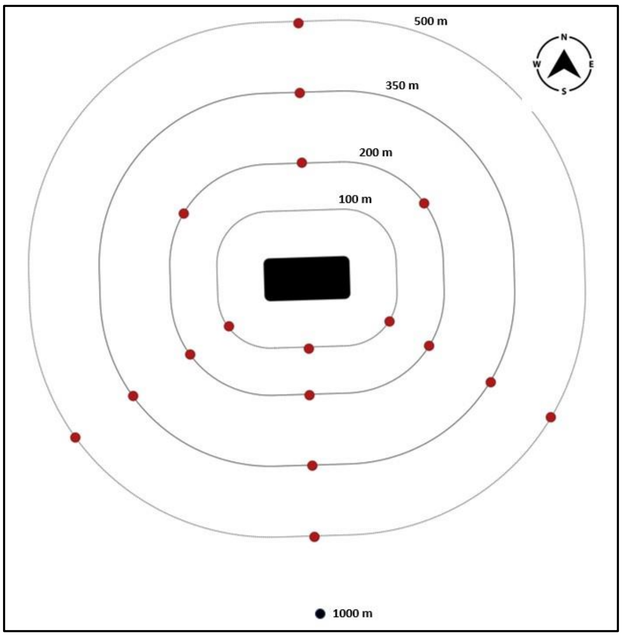

Figure 3. Sediment sampling stations monitored from 2010 to 2015 at several distances from the LNG terminal. Sampling station located 1000 m south (black dot) is not in scale.

Between 2011 and 2015, fish fauna was sampled twice a year, in late fall–winter (December–February). A professional fishing vessel was employed, and a fixed net (barracuda) was deployed at each site. The barracuda was 840 m total length, divided into four sections, each composed of panels with 20, 30, and 50 mm mesh size (Figure 4). Nets were kept fishing for 5 h, from 02:00 a.m. to 07:00 a.m. The catch, divided by mesh of capture, was analyzed once it arrived at the lab.

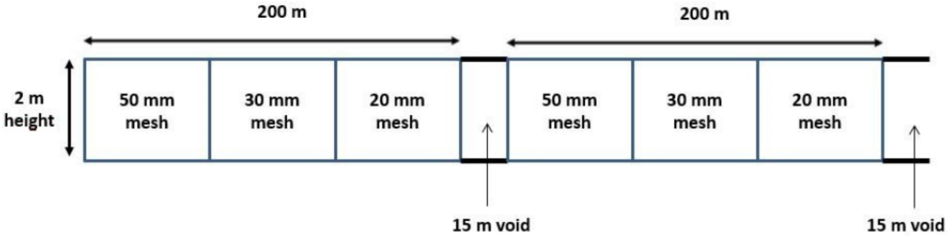

Figure 4. Fixed sampling net (barracuda) used for fish fauna sampling at the two sites. The scheme shows the arrangement of 2 sections out of 4 of a single net.

2.2. *Analysis of Disinfection Byproducts (DBPs)*

Analysis was carried out on seawaters, sediments, and tissues of mussels and fish muscle. Seawater samples were preserved and stored according to EPA methods [11–16].

Sediment samples were stored at –20 °C, then freeze-dried and homogenized before analysis; for VDbPs analysis, sediment was collected in a vial for purge and trap (P&T) and maintained at +4 °C until analysis.

Mussel, as well as fish muscles tissues were frozen at –20 °C, then freeze-dried and homogenized for the analysis of HAAs and HAPhs, except for VDbPs, for which they were collected in vials for head space (HS) and homogenized at 0 °C with an UltraTurrax before analysis.

2.2.1. Reagents and Chemicals

Mixtures of standard solutions of VDbPs (chloroform, bromodichloromethane, carbon tetrachloride, dibromochloromethane, bromoform, dichloroacetonitrile, trichloroacetonitrile, 1,1-dichloro-2-propanone, 1,1,1-trichloro-2-propanone, 1,2-dibromo-3-chloropropane, 1,1,1-trichloroethane, 1,2-dibromoethane, trichloroethene, tetrachloroethene), a mixture of HAAs (monochloroacetic acid—MCAA, monobromoacetic acid—MBAA, dichloroacetic acid—DCAA, trichloroacetic acid—TCAA, bromochloroacetic acid—BCAA, bromodich loroacetic acid—BDCAA, dibromoacetic acid—DBAA, chlorodibromoacetic acid—CDBAA, tribromoacetic acid—TBAA, Dalapon, 2,3 dibromo-propionic acid) and a mixture of HAPhs (4chloro-3-methyl-phenol, 2,4 dichloro-phenol, 2,4,6 trichlorophenol, pentachlorophenol) were purchased from Ultra Scientific, as well as the three single component solutions containing 2,4 dibromophenol, 2,5 di-bromotoluene, and 2,3 dibromopropionic acid. All solvents used were pesticide grade, purchased from Carlo Erba. Anhydrous sodium sulphate for residual pesticide analysis was obtained from Carlo Erba and further purified by heating at 400 °C for 4 h.

2.2.2. Volatile Disinfection Byproducts (VDbPs)

Analyses of VDbPs were performed according to EPA methods [11–13] adapted depending on the matrix to be analyzed. Instruments used for the analysis of VDbPs in seawaters and sediments were a P&T apparatus Eclipse 4660 equipped with an autosampler W&S 4552 (OI Analytical) coupled with a gas chromatograph (GC) 6890 mass spectrometer detector (MSD) 5973 (Agilent Technologies). For biota, analysis was carried out by a multisampler Gerstel MPS2 coupled with an Agilent Technologies GC 6890N-MSD 5975. Methods conditions and limits of quantitation (LOQ) are described in [7].

2.2.3. Haloacetic Acids (HAAs) and Dalapon

Chemical determination of HAAs in seawater, sediments, and biota was performed through a modified version of EPA methods [14,15] and described in [7].

Instrumental analysis was performed with an Agilent Technologies GC 6890 equipped with two electron capture detectors (ECD).

2.2.4. Halophenols (HAPhs)

Analysis was carried out with an Agilent Technologies GC 6890-MSD 5973 using a DB5MS-UI column (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness).

The analysis of halophenols in seawaters was carried out according to EPA methods [16,17].

Analyses from organism tissues and sediments were performed according to the abovementioned EPA methods, adapted, introducing the extraction phase from the different matrices.

A total of 1 g of organism tissue was added with 2,4-dibromophenol as surrogate and extracted with 20 mL of methanol in an ultrasound bath. The methanolic extract was collected in a 250 mL flask, diluted with 200 mL of deionized water and shaken with a magnetic stirrer. 5 mL of a potassium carbonate solution (600 g/L) and 5 mL of acetic anhydride were added to the solution and left under stirring for 5 min.The halophenols derivatized were extracted with 10 mL of n-hexane, stirring for 5 min. The organic extract was transferred to a flask and concentrated to a volume of 1 mL under a gentle stream of nitrogen. Internal standard 2,5-dibromotoluene was added before instrumental determination. Limit of quantitation for each compound was 5 ng/g w.w.

A total of 5 g of freeze-dried sediment added to a surrogate (2,4-dibromophenol) and 10 mL of solution HCl 0.1 M were extracted in an ultrasound bath for 30 min, then mechanically shaken for 30 min. After centrifugation, the solution was transferred to a collection flask. A second extraction was then carried out by adding 10 mL of a 0.1 M KOH solution and letting the vial sit in an ultrasonic bath for 30 min; subsequently the vial was shaken mechanically for another 30 min. After centrifugation, the solution was collected and transferred to the same collection flask. Two other successive acid-base extractions were then carried out, and the extracts were collected in the same collection flask. The collected extracts were then processed as described in [16].

The limits of quantification (LOQ) were the following: 2,4 dichlorophenol 1,2 ng/g d.w.; 4-chloro-3-methylphenol 1,1 ng/g d.w.; 2,4,6 trichlorophenol 1,4 ng/g d.w.; pentachlorophenol 1.6 ng/g d.w.

2.3. Statistical Methods

For comparative purposes, sediment concentration ratios (SCRs) for a *DBP* were calculated as reported by [18]. The calculation was as follows:

$$\mathrm{SCR}_{DBP} = [DBP_{Term.}]/[DBP_{\mathrm{Contr.}}] \tag{1}$$

where $[DBP_{Term.}]$ is the concentration of the contaminant (*DBP*) in sites near the terminal (from 100 to 1000 m) and $[DBP_{\mathrm{Contr.}}]$ the corresponding concentration of the contaminant (*DBP*) in the control sites (Contr.).

The same formula was adapted to calculate seawater concentration ratios (SWCRs) as follows:

$$\mathrm{SWCR}_{DBP} = [DBP_{Term.}]/[DBP_{\mathrm{Contr.}}] \tag{2}$$

where $[DBP_{Term.}]$ is the concentration of the contaminant (*DBP*) in sites near the terminal (*Term.*) (from 10 to 1000 m) and $[DBP_{\mathrm{Contr.}}]$ the corresponding concentration of the contaminant (*DBP*) in the control sites (Contr.).

To assess bioaccumulation of DBPs in transplanted mussels, bioaccumulation ratios (BARs) were calculated as follows:

$$\mathrm{BAR}_{DBP} = [DBP, T0]/[DBP, T1] \tag{3}$$

where [*DBP*, *T1*] is the concentration of each DBP in the organisms transplanted near the terminal (both on samples exposed to terminal effects and exposed to control sites) and [*DBP*, *T0*] the corresponding concentration of the contaminants in the organism before transplanting.

Values below LOQs were considered as $\frac{1}{2}$ LOQ for calculations and graphics. Mean values and confident levels (L-levels) were calculated for seawaters considering all the three levels together per sample, and for fish bioaccumulation considering all species collected in each sample. All sites were grouped per distance from the LNG terminal for graphical purposes.

3. Results

3.1. Seawater

Concentrations of VDbPs in seawater samples resulted almost all below LOQ, except for bromodichloromethane (0.051–0.053 µg/L, LOQ 0.010 µg/L), in both superficial and intermediate samples, collected in 2012 at 10 m and 50 m south of the terminal, dibromochloromethane (0.020 µg/L, LOQ 0.010 µg/L) in superficial water samples collected in 2011 and 2012, at 10 m south of the terminal, and bromoform (Figure 5) mostly at closer southern sites to the terminal from 10 to 20 m in 2011 and up to 100 m in 2012.

HAAs were detected at one deep sample, collected 100 m from the terminal in 2011 (MCAA 8.6 µg/L, LOQ 3.0 µg/L, MBAA 4.1 µg/L, LOQ 1.0 µg/L, Dalapon 1.1 µg/L, LOQ 1.0 µg/L, DBAA 0.8 µg/L, LOQ 0.5 µg/L), and at two superficial samples, the first collected 10 m away in 2011 (DBAA 2.1 µg/L, LOQ 0.5 µg/L), and the latter 100 m away in 2012 (DBAA 0.6 µg/L, LOQ 0.5 µg/L).

Other compounds were not detectable in all samples.

Table 1 shows the results of SWCRs.

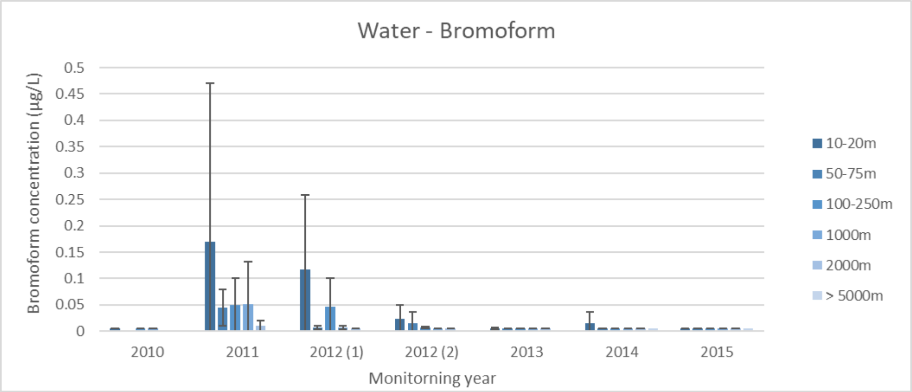

Figure 5. Bromoform concentrations in seawater samples (means ± L-levels) collected from 2010 to 2015 at different sites located away (10–20 m; 50–75 m; 100–250 m; 2000 m; over 5000 m) from the LNG terminal in the Northern Adriatic Sea. (1) July, (2) September. Note: LOQ 0.010 µg/L.

Table 1. Seawater concentration ratios (SWCRs) for bromoform resulted during monitoring activities of an LNG terminal in the Northern Adriatic Sea. (1) July, (2) September, nc = not calculated.

	Distance from the LNG Terminal			
Year	**10–20 m**	**50–75 m**	**100–250 m**	**1000 m**
2010	nc	nc	nc	nc
2011	16.9	4.5	5.0	5.1
2012 (1)	23.6	1.4	9.4	1.3
2012 (2)	4.8	3.2	1.4	1
2013	1.1	1	1	1
2014	3.15	1	1	1
2015	1	1	1	1

3.2. *Sediment*

DBPs detected in sediments were only HAAs. Figures 6 and 7 depict levels of DBAA and MCAA with values just above the respective LOQs. Both compounds were detected at the beginning of the survey, and they came back detectable again in 2015 with the improvement of analytical performances that strongly lowered LOQ values.

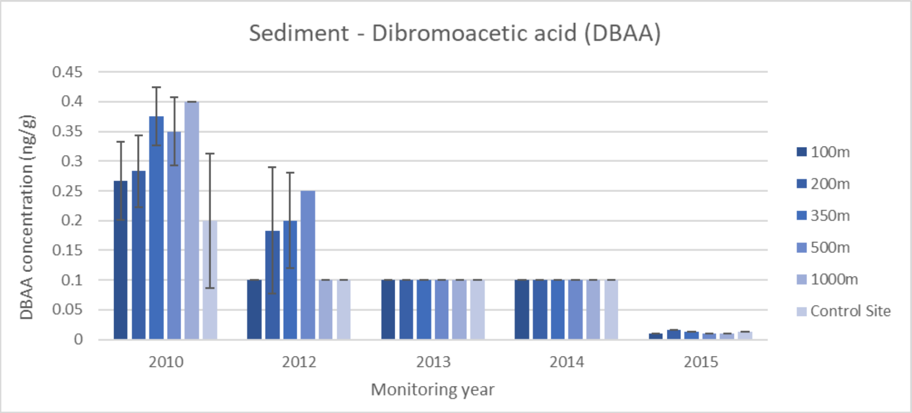

Figure 6. DBAA concentrations in sediment samples (means ± L-levels) collected from 2010 to 2015 at different sites located (100 m; 200 m; 350 m; 500 m; 1000 m) from LNG terminal and at control site in the Northern Adriatic Sea.

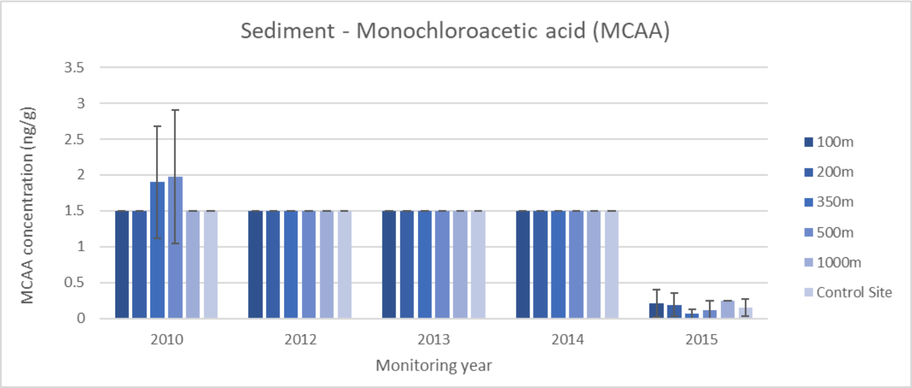

Figure 7. MCAA concentrations in sediment samples (means ± L-levels) collected from 2010 to 2015 at different sites located far (100 m; 200 m; 350 m; 500 m; 1000 m) from LNG terminal and at control site in the Northern Adriatic Sea.

Dalapon was present in very low concentrations (0.5 ng/g) slightly above the LOQ value (0.4 ng/g) in only one sample located 200 m far from the terminal in 2012. DCAA was detected in three samples at 100 m, 200 m, and control area (0.13 ng/g, 0.20 ng/g, and 0.15 ng/g, respectively; LOQ 0.06 ng/g) only in 2015, due to better performances of analytical methods. BCAA was detected in three samples at 200 m and 500 m away from the terminal (0.5 ng/g, 0.6 ng/g, and 0.6 ng/g, respectively) in 2012. CDBA was detected in only one sample (1.6 ng/g; LOQ 1.2 ng/g) at 500 m distance from the terminal in 2013.

SCR values are reported in Table 2.

Table 2. Sediment concentration ratios (SCRs) for DBAA and MCAA resulted during monitoring activities of an LNG terminal in the Northern Adriatic Sea. (1) July, (2) September.

		Distance from the LNG Terminal				
DBPs	**Year**	**100 m**	**200 m**	**350 m**	**500 m**	**1000 m**
DBAA	2011	1.33	1.42	1.88	1.75	2
	2012	1	1.83	2	2.5	1
	2013	1	1	1	1	1
	2014	1	1	1	1	1
	2015	0.75	1.25	0.94	0.75	0.75
MCAA	2011	1	1	1.27	1.32	1
	2012	1	1	1	1	1
	2013	1	1	1	1	1
	2014	1	1	1	1	1
	2015	1.35	1.25	0.41	0.78	1.63

3.3. Biota

Chloroform and DCAA were detected in several fish samples, mostly at the beginning of monitoring activities at both sites, in particular at the closer site located 300 m away from the terminal, except for DCAA in 2011 (Figures 8 and 9). Levels of chloroform (range 0.2–0.47 ng/g) were found in *Squalus acanthias* samples (0.47 ng/g and 0.42 ng/g in 2012, 0.3 ng/g and 0.2 ng/g in 2014), *Scomber scombrus* samples (0.38 ng/g in 2012, 0.3 ng/g and 0.2 ng/g in 2014), *Chelidonichthys lucerna* samples (0.4 ng/g in 2013), a *Mustelus mustelus* sample (0.29 ng/g in 2012), a *Diplodus annularis* sample (0.2 ng/g in 2013), and a *Solea solea* sample (0.2 ng/g in 2013). DCAA ranged from 4–9.5 ng/g in several *Squalus acanthias* samples from 2011 to 2012 with higher results on February 2011 (27.7 ng/g at control site). It resulted also in a *Solea solea* sample (7.8 ng/g in 2011), a *Scomber scombrus* sample (6 ng/g in 2012), and a *Mustelus mustelus* sample (4 ng/g in 2012). No haloacetonitriles were found in any samples, whilst 2, 4, 6 trichlorophenol levels were detected only in a *Scomber scombrus* sample in 2012 (6 ng/g). Finally, other haloacetic acids resulted in several samples, such as MCAA (12.6 ng/g in a *Squalus acanthias* sample in 2011), MBAA (14 ng/g and 10 ng/g in a *Spicara smaris* in 2013, and a *Squalus acanthias* sample in 2014), BCAA (1.4 ng/g and 1.5 ng/g at both sites in *Squalus acanthias* samples), and CDBAA (11.2 ng/g in a *Squalus acanthias* sample in 2011).

Chloroform and DCAA were also detected in some mussel samples, as well as MCAA (Figures 10–12). All these compounds were higher at the beginning of monitoring activities, with slightly higher levels at samples near to the terminal rather than control, except for chloroform in 2012 and 2013.

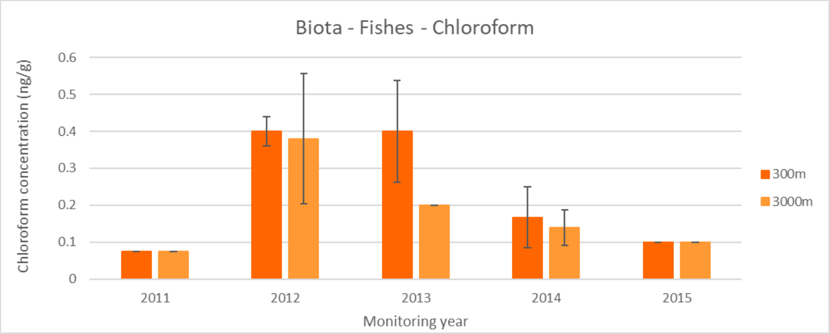

Figure 8. Chloroform concentrations (means ± L-levels) in fish samples collected from 2010 to 2015 at two sites located near the LNG terminal in the Northern Adriatic Sea.

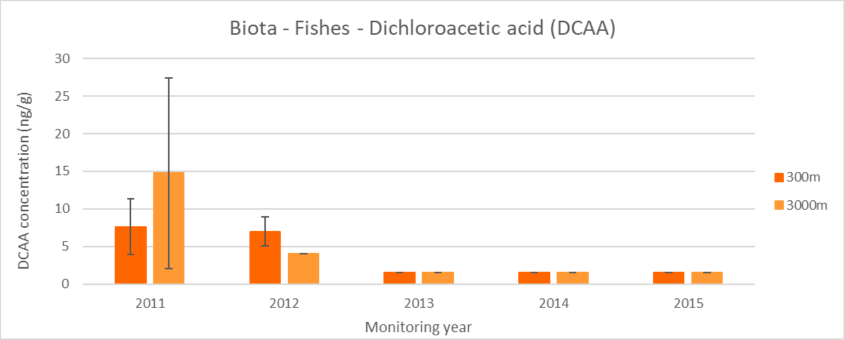

Figure 9. DCAA concentrations (means ± L-levels) in fish samples collected from 2010 to 2015 at two sites located near the LNG terminal in the Northern Adriatic Sea.

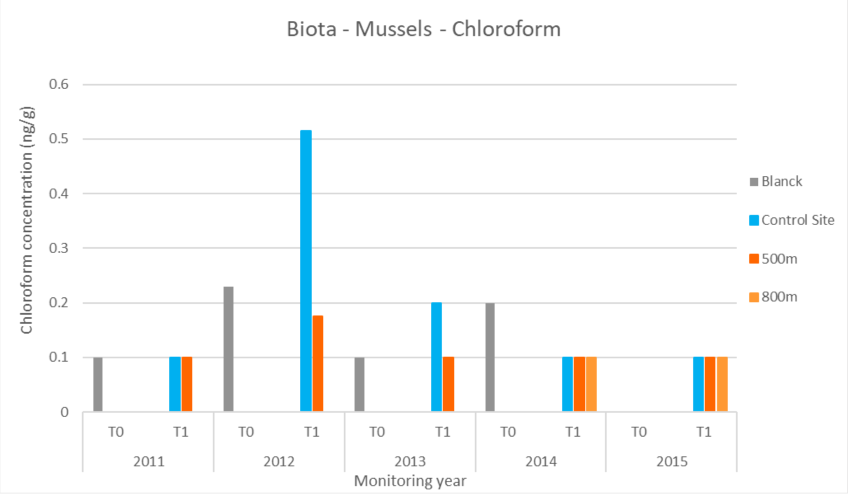

Figure 10. Chloroform concentrations in mussel samples collected from 2010 to 2015 at sites located near the LNG terminal and at control site in the Northern Adriatic Sea.

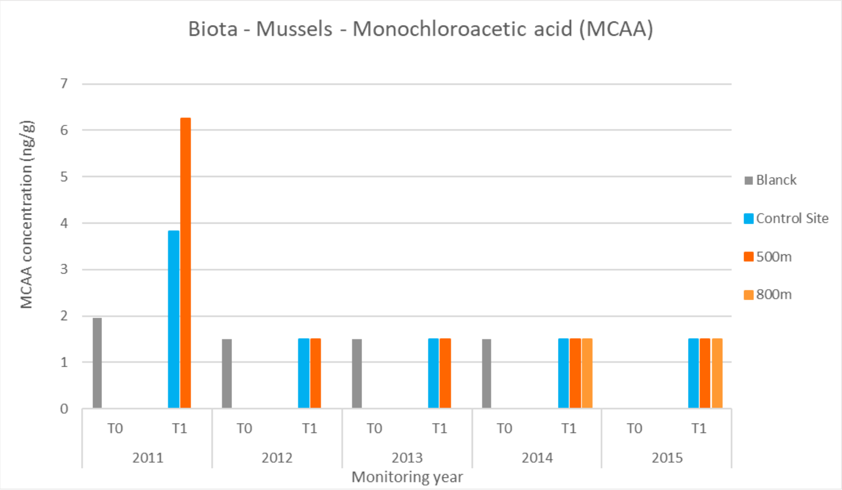

Figure 11. MCAA concentrations in mussel samples collected from 2010 to 2015 at sites located near the LNG terminal and at control site in the Northern Adriatic Sea.

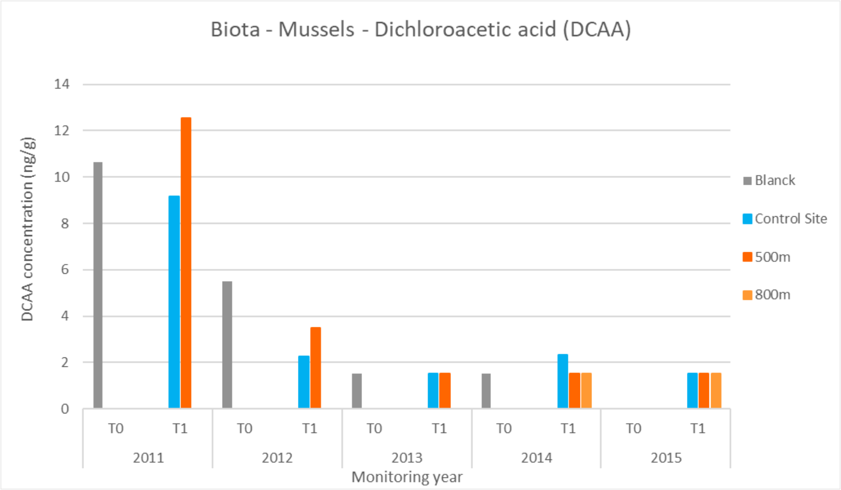

Figure 12. DCAA concentrations in mussel samples collected from 2010 to 2015 at sites located near the LNG terminal and at control site in the Northern Adriatic Sea.

BAR values are shown in Table 3.

Table 3. Bioaccumulation ratios (BARs) for chloroform, MCAA, and DCAA resulted during monitoring activities of an LNG terminal in the Northern Adriatic Sea.

		Distance from the LNG Terminal		
DBPs	**Year**	**Control Site**	**500 m**	**800 m**
Chloroform	2011	1	1	
	2012	2.24	0.76	
	2013	2	1	
	2014	0.5	0.5	0.5
MCAA	2011	1.96	3.21	
	2012	1	1	
	2013	1	1	
	2014	1	1	1
DCAA	2011	0.86	1.18	
	2012	0.41	0.64	
	2013	1	1	
	2014	1.56	1	1

4. Discussion

The present study is the first one displaying results of DBPs in the proximity of a regasification LNG terminal in the Adriatic Sea.

Among all DBPs analyzed in seawaters, bromoform was the compound most frequently detected, as previously found in other studies on chlorinated seawaters [7,19–24]. In a baseline study reporting DBP levels associated with oxidant treatment of ballast waters in seven ports of the Adriatic Sea, bromoform concentrations in seawaters ranged from <0.01 to 0.90 µg/L [7]. In our study, bromoform levels ranged from <0.01 to 0.17 µg/L and the compound was found in the first surveys (2011–2012) at the closest sites to the terminal, but it definitely lowered all over the monitoring area in the following years. Two other compounds (bromodichloromethane and dibromochloromethane) were rarely found in seawaters, slightly above LOQ, only during the first years of the survey (2011 and 2012) and near the LNG terminal, also confirmed by SWCR values.

Sediments were mostly characterized by HAA presence, such as DBAA, MCAA, DCAA, BCAA, and CDBA, with values generally close to the respective LOQs. In addition, Dalapon was also detectable. However, only DBAA was present at almost all sites, except for the control site, at the beginning of the surveys. These compounds are commonly found in sediments near platforms or wastewater using chlorine for disinfections [7,20,21]. Substrate texture has an important effect on the types of DBPs adsorbed in the sediments, with sandy samples mostly characterized by the presence of HAAs, rather than VDbPs [3]. Grain-size composition of sediments near the LNG terminal were quite heterogeneous, even if they were all sandy, varying from very coarse sand in the nearest sites to silt fraction ranging 44–22 µm at 200–500 m away from the terminal. Control sediment grain size was very different from the other sites, with homogenous medium sand in all samples and surveys [1]. These differences in grain-size composition may explain higher accumulation of DBAA and MCAA at sites placed 350–1000 m away from the terminal. However, levels of HAAs were mostly negligible or slightly above LOQs, except for the first years of sampling. SCRs showed quite homogenous values during surveys and sites.

Chloroform levels were detected both in mussels and in muscles of fish fauna, even if bromine should be more prevalent than chlorine as a halogen found in marine biota [4]. However, the highest levels of chloroform of the present study were found in mussel samples rescued from the control site both in 2012 and 2013, which means that it could be not directly related to terminal wastewater exposition.

Results in biota showed patterns similar to those found in sediments, with bioaccumulation of HAAs higher than the other DBPs. DCAA was detected, indeed, both in fish fauna and in mussels, whilst MCAA was detected only in mussels. BARs were quite homogeneous between sites and surveys as well as in sediments. When BARs are higher than SCRs, this indicates bioavailability of contaminants [18]. The finding that BARMCAA was slightly higher than SCRMCAA can also support that sediment may be the main source of contamination in mussels, probably due to resuspension dynamics. However, concentrations found in this study were very low, with comparable values between the terminal and control area, and little data exists on bioavailability of DBPs in mussels and fish fauna from sediments.

Among fish fauna, *Squalus acanthias* showed the highest levels of DBPs of the present study and had similar compounds to those found in sediments. These results could be linked with the feeding behavior of the species, which prey mainly on benthic fishes. Further investigation is necessary to provide data on bioaccumulation and bioavailability of DBPs from sediment, especially using benthic bioindicators.

5. Conclusions

The active chlorine concentration in the discharged seawater of the LNG terminal in the Northern Adriatic Sea is within limits set by Italian regulations; however, a specific monitoring program was scheduled from 2010 to 2015 to verify the possible presence of DBPs in the marine environment. During this monitoring period, it was possible to detect some DBPs in different matrices, with quite low levels, slightly above LOQs, in the area close to the terminal just in the first two monitoring surveys. In the subsequent years of monitoring activities, levels of DBPs were mostly negligible. More detectable compounds were bromoform in seawaters (<0.01–0.17 µg/L), DBAA and MCAA in sediments (<0.02 to 0.4 ng/g and <0.06–1.98 ng/g, respectively), chloroform and DCAA in fish fauna and mussels (<0.15–0.40 ng/g and <3–14.7 ng/g in fish fauna, <0.2–0.5 ng/g and <3–12.6 ng/g in mussels, respectively) and MCAA in mussels (<3–6.25 ng/g).

This study demonstrates the importance of carrying out environmental monitoring programs lasting several years in order to verify the time evolution of potential environmental impacts.

Furthermore, the present study represents a baseline for the different DBPs in the environmental matrices (seawaters, sediments, and biota) in Adriatic Sea, as no data are available, except for port monitoring for ballast water effects [7].

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