



The disinfection by-products are in the air: Aerosol measurements in the urban area of Venice

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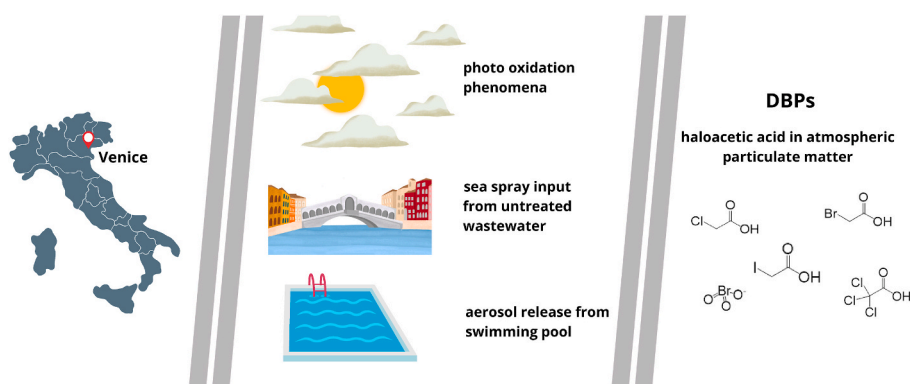
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HIGHLIGHTS

- A sensitive method was developed for fourteen HAAs in atmospheric aerosol.
- The presence of iodinated organic acids was also evaluated.
- Sea spray and atmospheric photo oxidation are the main source of HAAs.
- The presence of a swimming pool slightly impacted in the airborne HAAs load.

GRAPHICAL ABSTRACT



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ABSTRACT

Haloacetic acids (HAAs) are usually taken to be man-made, regularly determined in drinking water as disinfection by-products; yet they have been demonstrated as a probable photooxidation products from atmospheric halogenated hydrocarbons. Here we determined a total of fourteen HAAs, including for the first time iodinated-HAAs, in aerosol samples collected from April to June 2023 at Parco Bissuola (urbanized area of Venice) and Rio Novo (Venice island). The study provides a first insight and source identification about the anthropogenic or natural origin of HAAs. To fulfil this aim, we improved existing methods with a highly sensitive technique by using high pressure anion exchange chromatography coupled to a triple quadrupole mass spectrometer. Five HAAs have been found to be above the detection limits at both sites, and the major source should be attributed to a mixed contribution from atmospheric oxidation of both organic precursor, sea spray and a minor contribution of an external swimming pool located near the Parco Bissuola site. Considering the presence of iodinated HAAs and their cytotoxicity, the present study also provides a basis for the assessment of risks for humans.

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1. Introduction

The evolution to an urbanized civilization has increased the anthropogenic inputs, economic growth, industrialization, resulting in massive waste management, and disposal problems. Among other matrices, atmosphere is one of the most influenced by the growing number of contaminants of emerging concern (CECs) and related by-products (Yadav et al., 2021). By-product of some compounds that are released by humans may be more significant due to their emerging importance. Haloacetic acids (HAAs) could be present in the atmosphere as a by-product of anthropogenic volatile precursors (Ellis et al., 2001). Some studies (Ellis et al., 2001; Frank et al., 1995; Mashino et al., 2000) report how HAAs may be released by the oxidation of halogenated C2-hydrocarbons. Despite during the 1990s there was a strong declining emission of halocarbons in the atmosphere by the effects of the Montreal Protocol, dichlorodifluoromethane and 1,1,2-trichloro-1,2,2-trifluoroethane did not respond to decreasing emissions source (Hodnebrog et al., 2013), probably due to their lifetimes of 100 and 85 years, respectively. Frank et al. (1995) found how chlorinated and brominated acetic acids were always detectable in the urban air of Germany, with monochloro acetic acid being the most concentrated HAA. These relative abundance of HAAs matched the profile in air also observed by Martin et al. (2003) in Canada. HAAs are also formed as disinfection by-products (DBPs) after water disinfection. Thus, the disinfectants can react with organic matter and inorganic ions (e.g., bromide and iodide) to form DBPs. The first report about DBPs in swimming pool water was the study of trihalomethanes (THMs) in swimming pool water in 1980s (Beech et al., 1980), while the occurrence of HAAs in swimming pool water was detected for the first time in 1999 (Martínez et al., 1999). Other possible sources of HAAs are the breakdown of fluorinated pesticides or waste incineration (Römpp et al., 2001). Bromoacetates are suggested to be released by atmospheric degradation of brominated hydrocarbons emitted by marine organisms (Römpp et al., 2001). Some studies suggest also that trichloroacetic acid can be formed from humic acids in the chloroperoxidase-mediated reaction and chloroperoxidase-like activity in soil (Hoekstra et al., 1999), nevertheless, the strengths of this source is difficult to assess.

Currently, five HAAs are regulated by the U.S. EPA and E.U. The maximum level in drinking water is fixed at $60 \mu\text{g L}^{-1}$ as a sum of chloroacetic, bromoacetic, dichloroacetic, dibromoacetic and trichloroacetic acids. Bromate is currently regulated at $10 \mu\text{g L}^{-1}$ in the U. S. and E.U. Toxicological studies have proven that HAAs, including bromate, are genotoxic, cytotoxic and may induce DNA damage (Richardson et al., 2007). Some of the unregulated chemicals are like those that are regulated, such as other HAAs or iodinated HAAs. Previous studies on HAAs in water focused on bromo-HAAs and chloro-HAAs, while iodo-HAAs with higher toxicity were less concerned than Cl/Br-HAAs (Plewa et al., 2004).

Some studies reported that the concentrations of HAAs in swimming pool water are higher than that in tap water (Hang et al., 2016; Simard et al., 2013) mainly due to the higher presence of halide, disinfectants, and multiple types of organic matter. Furthermore, the accumulation period due to the water circulation and recycling result in the higher concentrations of HAAs in swimming pool (Weisel et al., 2009). The presence of seawater, which has a high content of dissolved organic material, chloride and bromide, can generate brominated HAAs (Parinet et al., 2012). Such impact may be enhanced by the total absence of sewage treatment systems with the direct introduction of chlorinated water in the environment (Manasfi et al., 2016; Qi et al., 2019).

Data on atmospheric presence of HAAs is essential to predicting their future deposition trends and to understand how different sources can change their airborne concentrations. Most of the time HAAs have been characterized in fog and rain (Berg et al., 2000; Reimann et al., 1996), but surprisingly the atmospheric sources of HAAs are poorly described despite their airborne presence is confirmed (Martin et al., 2003). Thus, the generation of atmospheric MCAA and DCAA has been hypothesized

to result from photochemical reactions, primarily through correlations with short-wave radiation (Martin et al., 2003). Nevertheless, the specific precursor compounds responsible for these reactions remain unidentified. There is no information about the source and reactions pathway for the rest of HAAs. No legislation was passed regarding the maximum concentration levels of HAAs in air. Scarce information is reported regarding the inhalation exposure for HAAs and most of them are focused on indoor exposure during swimming or showering (Cardador and Gallego, 2011; Levesque et al., 2006; Parvez et al., 2019; Xu and Weisel, 2003), while HAAs exposure in aquatic environment have been widely investigated (Li et al., 2022). Therefore, the present study aims to highlight the emerging concern about the presence of chlorinated, brominated, and iodinated HAAs in $\text{PM}_{2.5}$ atmospheric aerosol. The determination of HAAs in $\text{PM}_{2.5}$ comes from observational of people exposed to different levels of air pollution, showing particularly effects of long-term $\text{PM}_{2.5}$ exposure on cardiovascular disease (Hayes et al., 2020).

The aim of this work is to investigate in the aerosols of Venice the presence of fourteen HAAs, eleven of them are included in the EPA method 557: Determination of haloacetic acids, bromate, and dalapon in drinking water by ion chromatography electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS). The presence of HAAs in $\text{PM}_{2.5}$ is an emerging concern as it underscores the complex interplay between air, water, and photochemistry, which has not been extensively explored. The interest of studying a broad range of HAAs in the atmosphere lies in their potential to expand our knowledge of uncover new health risks. Hence, the study provides a first insight about anthropogenic or natural origin of HAAs. For the first time we determined iodinated HAAs in $\text{PM}_{2.5}$, aiming to understand their load to figure out their contribution in the atmosphere, considering their cytotoxicity (Hu et al., 2018b).

2. Experimental

2.1. Materials and method

Monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), bromate (Br O_3^-), dalapon (DA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), tribromoacetic acid (TBAA), diiodoacetic acid (DIAA) and cloroiodoacetic acid (CIAA) were purchased from LGC Standard (Teddington, UK). Bromate (Br O_3^-) and monoiodoacetic acid (MIAA) were purchased from Merck KGaA (Darmstadt, Germany). The internal standard monochloroacetic acid-2- ^{13}C (MCAA-ISTD), monobromoacetic acid-1- ^{13}C (MBAA-ISTD), dichloroacetic acid-2- ^{13}C (DCAA-ISTD) and trichloroacetic acid-2- ^{13}C (TCAA-ISTD) were purchased from Thermo Fisher Scientific (Waltham, USA). Structures of all HAAs are shown in Table S1. Ultra-grade methanol (MeOH) was purchased from VWR® (Radnor, PA, USA) and ultrapure water was produced using a Purelab Ultra System (Elga®, High-Wycombe, UK) (18.2 $\text{M}\Omega\text{-cm}$, 1 ppb TOC). Ultrapure methanol (MeOH) was purchased from VWR Chemicals (Radnor, Pennsylvania, USA). Sampling in both sites was performed using a Skypost $\text{PM}_{2.5}$ sampler (Tecora™, Monza-Brianza, Italy) equipped with a sequential system of 47 mm diameter quartz fiber filter (Filter Lab, Barcelona, Spain). Meteorological data were provided by ARPAV (arpa.veneto.it/dati-ambientali/dati-storici/meteo-idro-nivo/ulti-mi-anni) extracted from the station 252 located in Venice Island ($45^\circ 25' 47.8'' \text{ N } 12^\circ 19' 41.1'' \text{ E}$).

2.2. Sampling sites

The aerosol samples were collected in due different sites in the Venice urban area (Veneto Region, Italy), on the extreme East side of Po' Valley. Parco Bissuola site (PB, $45^\circ 29' 58.7'' \text{ N } 12^\circ 15' 40.5'' \text{ E}$) is located in a public park extending for 0.4 km^2 . It receives pollution only indirectly

mainly from fallout and is a source of crustal dust from the soil (Ram-pazzo et al., 2008). It is located 4 km far from the Venice Lagoon. Furthermore, the site was selected because is located about 50 m far from an outdoor swimming pool (Fig. 1). PB can provide insights about the possible presence of HAAs in $PM_{2.5}$ in a high frequented area such as public park. Rio Novo site (RN, $45^{\circ}26'8.0''N$ $12^{\circ}19'23.3''E$) is placed into the Venice Island, signifying an intense water-traffic area. Venice is characterized by the absence of treatment plants for wastewater discharge, and this enhances the presence of pollutants in the Venice Lagoon. The sampling campaigns lasted from 4th April to 12th June at PB and from 3rd April to June 4, 2023 at RN. For each station we performed a systematic random sampling to select two samples per week for each station. Sampling resolution was set at 24 h with a flow rate of 38.3 and 16.7 L min^{-1} with an average final volume for each filter of 55 and 24 m^3 for PB and RN, respectively. Blank samples were collected by loading a filter into the instrument for a couple of minutes.

2.3. Sample processing, instrumental analysis and quality control

The aerosol was collected on 47 mm quartz fiber filters with the support of the Environmental Agency of Veneto Region (ARPAV). After sample collection, the filters were stored at -20°C . The filters were then broken up with steel tweezers, spiked with internal standard (100 absolute ng of each labelled ISTD) and placed in 10 mL vial (previously cleaned with ultra-pure MeOH). The samples were cold-ultrasonically extracted for 30 min after addition of 10 mL of ultrapure water. The extract was filtered through a 0.45 mm polytetrafluoroethylene (PTFE) filter (Biocomma, Guangdong, China) to remove particulates traces before analysis. All the operation were performed under a laminar flow bench. To minimize the instrumental fluctuations, the results were corrected using a response factor by analysing a standard solution prepared in ultrapure water with a mean concentration of $10 \mu\text{g L}^{-1}$.

Determination of HAAs was performed using a HPAEC (DionexTM, Thermo ScientificTM, ICS-5000, Waltham, USA) coupled to a TSQ AltisTM Plus Triple Quadrupole Mass Spectrometer (Thermo ScientificTM, ICS-5000, Waltham, USA) using a heated-electrospray source (H-ESI) that operated in negative mode. Chromatographic separation was performed using an anion exchange column Dionex IonPacTM AS24 RFICTM 2×250 mm (Thermo ScientificTM) equipped with a guard column Dionex IonPacTM AG24 RFICTM 2×50 mm (Thermo ScientificTM). The chromatographic gradient achieved with potassium hydroxide, as mobile phase, and separation are shown in Supporting Information (Figs. S1 and S2, respectively). The mass spectrometer's and source's parameters are

shown in Tables S2 and S3, respectively.

QA/QC was performed by comparing the compound peak areas with that of the internal standards, MCAA-ISTD, MBAA-ISTD, DCAA-ISTD and TCAA-ISTD. The abovementioned analytical procedure was validated by determining the linear ranges from 5 ng L^{-1} to $30 \mu\text{g L}^{-1}$, procedural blanks, instrumental limits of detection (LOD), instrumental limits of quantification (LOQ), method detection and quantification limits (MDL and MQL), repeatability and trueness (Thompson et al., 2002). The LOD and LOQ values were calculated as three and ten times the signal-to-noise ratio of the determinations of the known absolute amounts of the analysed target compound in the standard solution. The scarce literature on the presence of HAAs does not provide information about the limits of quantification in aerosols. Because of the lack of certified reference materials of urban aerosol for the determination of trueness and precision of HAAs, we calculated them by analysing five filters spiked with 100 absolute ng of native HAAs. Table 1 shows the internal standard assignment used for the validation procedure, linearity coefficient, slope, intercept, LOD, LOQ, blank levels, MDL, MQL, trueness, recovery and precision expressed as the relative percentual standard deviation (also known as coefficient of variation, CV%).

The MDL and the MQL were evaluated as 3 and 10 times the standard deviation of the blank results (Bliesner, 2006). Our MDL values are about one order of magnitude lower than those reported by Martin et al. (2003), who reported MDLs of 100 pg m^{-3} for MCAA, 50 pg m^{-3} for DCAA and 46 pg m^{-3} for TCAA with a sampling volume of 48 m^3 . Considering the mean sampling volumes of PB (55 m^3) and RN (24 m^3), we obtained MDLs of 7 pg m^{-3} and 52 pg m^{-3} for MCAA, 0.1 pg m^{-3} and 1 pg m^{-3} for DCAA, and 4 pg m^{-3} and 27 pg m^{-3} for TCAA at each site respectively.

The matrix effect (ME) in percent is obtained by comparing the signal responses of each standard present into a synthetic sample spiked with three different concentrations (5 , 10 and $20 \mu\text{g L}^{-1}$) and those obtained by injection of standards in ultrapure water. The synthetic sample extract was made by sonication of a quartz filter and 2 mg of NIST1649B urban dust certified material (Merck KGaA, Missouri, USA) with 10 mL of ultrapure water. A value $< 100\%$ is indicative of an ionization suppression, while values close to 100% suggest that matrix effect is negligible (Matuszewski et al., 2003). A slight suppression was found for each HAA at the three concentrations with ME values always above 80% while a small enhancement was determined for MIAA at $5 \mu\text{g L}^{-1}$ (113%) and at $10 \mu\text{g L}^{-1}$ (101%) (Table S4).



Fig. 1. Sampling site's locations in Venice.

Table 1Internal standard assignment, R², slope, intercept, LOD, LOQ, blank levels, MDL, MQL, trueness, recovery, and precision of each compound.

Compound	ISTD	R ²	Slope	Intercept	LOD (ng L ⁻¹)	LOQ (ng L ⁻¹)	Blank (ng)	MDL (ng)	MQL (ng)	Trueness (%)	Recovery (%)	Precision (CV %)
MCAA	MCAA-ISTD	0.9993	0.8087	0.0105	0.7	2.4	1.36	0.37	1.24	-9	84	4
MBAA	MBAA-ISTD	0.9999	0.2853	0.0043	3.1	10.4	1.83	0.23	0.78	-9	81	5
MIAA	MBAA-ISTD	0.9998	1.048	-0.0101	8.5	28.5	0.08	0.02	0.06	-9	76	3
DCAA	DCAA-ISTD	0.9996	0.8514	0.0065	1.2	4.2	0.03	0.01	0.02	-3	78	3
DBAA	DCAA-ISTD	0.9997	1.211	-0.0122	5.9	19.7	0.04	0.004	0.014	-9	72	3
BCAA	DCAA-ISTD	0.9995	0.2171	-0.0034	26.4	87.9	0.10	0.02	0.07	-6	76	3
DIAA	DCAA-ISTD	0.9994	2.1066	-0.0137	4.4	14.8	0.03	0.01	0.03	-10	70	1
CIAA	DCAA-ISTD	0.9997	0.8174	-0.0095	3.0	9.9	0.02	0.002	0.007	-9	72	4
TCAA	TCAA-ISTD	0.9996	0.8500	0.0114	4.9	16.3	0.75	0.19	0.64	3	91	4
TBAA	TCAA-ISTD	0.9991	0.0382	0.0026	255	850	8.88	1.43	4.77	-5	79	6
CDBAA	TCAA-ISTD	0.9978	1.2293	-0.0135	31.0	103	0.54	0.03	0.10	-6	82	4
BDCAA	TCAA-ISTD	0.9998	2.0201	-0.0036	30.6	102	0.33	0.05	0.16	-1	86	4
DA	DCAA-ISTD	0.9996	0.4184	-0.0056	11.9	39.7	0.14	0.02	0.06	-5	75	3
Br O ₃ ⁻	MBAA-ISTD	0.9993	3.3721	0.0225	1.5	5.0	0.002	0.0004	0.0013	6	106	5

3. Results and discussion

3.1. Sites comparison

MCA, MBA, MIA, Br O₃⁻ and TCA were found in the urban aerosol, while the other HAAs were always below the detection limits. The mean concentrations of the detected HAAs in the Venice PM_{2.5} samples are given in Table 2. These relative abundance are similar to those found in Tübingen, Germany (Frank et al., 1995) and in Toronto, Canada (Martin et al., 2003). Despite PB may be impacted by the presence of an external swimming pool, due to the presence of body fluids and personal care products from the swimmers in addition to the natural organic matter that result in the abundant formation of HAAs (Zhao et al., 2020), and RN by the untreated wastewater of Venice Island, the mean values of HAAs are comparable. The only significant difference is given by MBAA that show concentration five times greater in RN. There may be two possible explanations for this similarity: 1) the external swimming pool at PB and the absence of wastewater treatment in Venice likewise impacted in the PM_{2.5} or 2) the mentioned possible short-range sources are not the most impactful and other inputs need to be considered.

3.2. Sources of HAAs

Previous studies showed that the presence of MCAA, DCAA and TCAA in the environment may be released from oceans or from various atmospheric photo-oxidation (Scott et al., 2005). Thus, MCAA seems to

Table 2Mean values (ng m⁻³) for detectable HAAs. Standard deviations are reported in brackets.

	PB	RN
MCAA	0.2 (0.2)	0.3 (0.2)
MBAA	0.01 (0.01)	0.05 (0.02)
MIAA	0.01 (0.01)	0.02 (0.01)
Br O ₃ ⁻	0.0005 (0.0003)	0.0001 (0.0002)
TCAA	0.01 (0.01)	0.02 (0.01)

follow various oxidation pathways involving chlorine radicals, trichloroethylene, 1,2-dichloroethene, and vinylchloride while TCAA has been shown to be released by oxidation of the C2-chlorocarbons tetrachloroethene and 1,1,1-trichloroethane within the planetary boundary layer (Frank et al., 1994).

In this case study, MCAA reached the highest values in both sites in the end of May or first days of June (Fig. 2). The observed temporal trends are consistent with previous studies, showing that MCAA was much higher in April and June than in rest of the year (Frank et al., 1995; Martin et al., 2003). Thus, photochemical reactions have previously been suggested as a source of atmospheric MCAA (Reimann et al., 1996), however no correlations were found between MCAA and meteorological parameters (temperature and global solar radiation). The correlation between HAAs and precipitation was negligible due to the low rainfall event during the sampling period that generated low precipitation data (Fig. 3). It has to be noted that the global solar radiation reached the highest values (Fig. 2) during the maximum concentrations of MCAA, this probably increased the consumption of organohalogen precursors promoting the formation of MCAA.

Römpf et al. (2001) found that MBAA in fog was associated with marine air and possible precursors could be brominated hydrocarbons that are produced by marine algae (Gribble, 1999). Considering that RN site is located in the middle of the Venice Lagoon, the greater concentration of MBAA (Table 2) in RN compared to PB may be attribute to the sea spray phenomenon.

It has been reported that iodinated DBPs are more toxic than brominated and chlorinated HAAs (Hu et al., 2018a). MIAA shows a constant trend in both sites, even if in RN it was again more concentrated. This may be related to the emission of organic iodine species due to the increasing algae populations during spring and summer (Yu et al., 2019). The marine source is supported by a significative correlation between MBAA and MIAA (Fig. 3) at RN, while correlation between MIAA and MBAA wasn't significant at PB because of the greater distance from the sea. MIAA positively correlated with MCAA, suggesting a lower marine impact for MIAA there and a more likely atmospheric photo-degradation pathway. To the best of our knowledge, this is the first determination of MIAA in the atmosphere and our findings can fill the

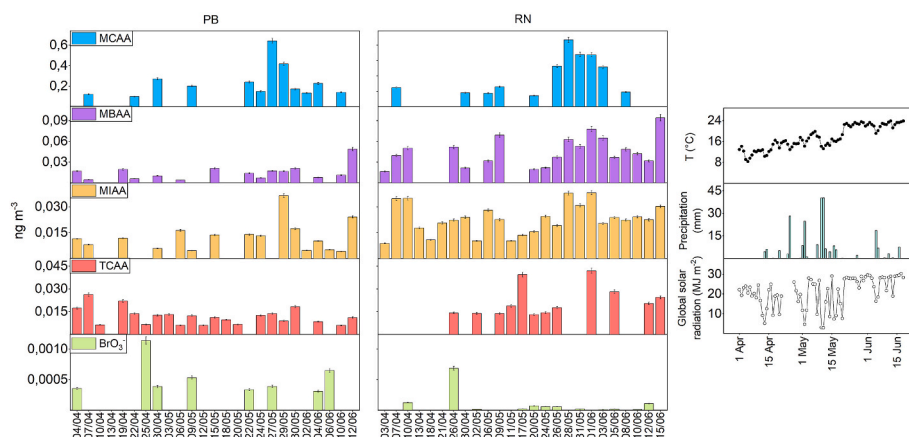


Fig. 2. Temporal trend of HAAs at PB and RN (left), meteorological parameters (temperature, precipitation, and global solar radiation) (right). Error bars were calculated using the CV% showed in Table 1.

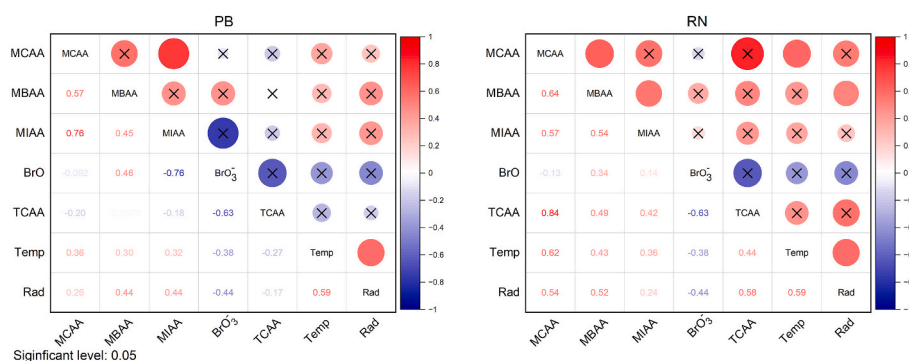


Fig. 3. Correlation plots for PB and RN. In the upper and lower triangular the insignificant mark and the correlation coefficients are respectively reported.

gap regarding the type of iodinated organic adduct generated by algae growth.

TCAA occurs at concentrations of about a tenth of MCAA, as reported by Frank et al. (1995). Considering the proximity to the sea of both sites, C2-chloroorganics (being probably present in the Lagoon, taking into account the lack of wastewater treatment plants) are oxidized by hydroxyl radicals during air transport to form TCAA, as reported for the Caspian Sea (Weissflog et al., 1999). Furthermore, TCAA did not correlate with other HAAs or meteorological parameters, but literature suggests that the presence of TCAA in the atmosphere can be explained by anthropogenic precursors (Scott et al., 2005).

Br O₃ was almost absent in the examined sites. The source in PM_{2.5} can be dual: 1) Br O₃ can certainly be released by untreated wastewater or swimming pool, as found elsewhere (Righi et al., 2014); 2) Br O₃ may be a by-product of naturally occurring bromide in the atmosphere because of the presence of hydroxy radicals or ozone, with similar atmospheric mechanisms followed by Cl O₃ and Cl O₄ (Feltracco et al., 2022; Jackson et al., 2018).

4. Conclusion

To the best of our knowledge, this is the first study that provides a basis for interpretation of the presence of haloacetic acids, including iodinated-HAAs, in atmosphere. Besides common HAAs, we have detected for the first time MIAA and Br O₃ in urban PM_{2.5} of Venice, indicating that these compounds can have different sources, depending on the characteristics of the atmosphere and the meteorological conditions. Furthermore, a new highly sensitive analytical method was developed to simultaneously analyse HAAs in aerosol. The major source detected were likely the photooxidation from halocarbon precursor or

sea spray and the solar radiation may certainly enhance this process. Although the PB site is located about 50 m far from an external swimming pool, its impact on the HAAs occurrence in the atmosphere is probably negligible.

CRediT authorship contribution statement

Matteo Feltracco: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Elena Barbaro:** Writing – original draft, Writing – review & editing. **Gianni Formenton:** Data curation, Investigation, Methodology, Writing – review & editing. **Giovanna Mazzi:** Writing – original draft, Writing – review & editing. **Sveva Striuli:** Data curation, Formal analysis, Methodology, Validation, Writing – review & editing. **Carlo Bragato:** Supervision. **Rossano Piazza:** Supervision. **Carlo Barbante:** Supervision, Writing – review & editing. **Andrea Gambaro:** Conceptualization, Investigation, Supervision, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2023.120224>.

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