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Occurrence of tyre-derived particles in size-segregated aerosol in the urban area of Venice

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HIGHLIGHTS GRAPHICAL ABSTRACT

- Quantification via UHPLC-MS/MS of eight BTHs in size-segregated urban aerosol.
- Characterization of BTHs' distribution across twelve particle size fractions.
- Rooftop level aerosol composition as reflective of the urban background layer.
- BTHs diagnostic ratios as possibile markers for photochemical processes.

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ABSTRACT

Benzothiazoles (BTHs), commonly used in various industrial applications, have emerged as significant contaminants due to their widespread usage and potential adverse effects on ecosystems and human health. The aim of this study is to quantify and, for the first time, to characterize the particle size distribution of eight BTHs across twelve fractions of atmospheric aerosol representative of the urban boundary layer. Samples were collected from August to October 2023 in the urban area of Venice, located in the Po Valley, known for its poor air quality. Instrumental analysis was achieved via an UHPLC system coupled with a triple quadrupole mass spectrometer.

All target compounds were present in the samples analyzed and most of them tended to distribute mainly in the fine fraction of aerosol (<1.8 μm). An exception is given by BTH-SO₃H, which presents a bimodal distribution with maxima centered in the coarse fraction; this may imply a different source compared to other BTHs. BTH-SH is the most abundant benzothiazole derivative, suggesting tyre debris as the main source since it is the main

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compound used in vulcanizing accelerators in rubber manufacture. Given its mutagenic properties, its high relative abundance could be of concern for human health.

Results: of this work provide valuable insights into the distribution of BTHs in urban aerosols, laying the groundwork for future research aimed at better understanding their sources and environmental pathways, fate and impacts.

1. Introduction

In the last decades, rapid urbanization and industrial and economic growth have led to the acceleration of the anthropogenic impact on the planet. The emission in the environment of Chemicals of Emerging Concern (CECs) is consistently increasing, hence their monitoring is of growing interest for the scientific community and policy makers. Among other environmental compartments, the atmosphere is one of the most affected by the growing number of CECs, as they are still poorly regulated and not extensively monitored ([Yadav et al., 2021](#page-6-0)). The Italian legislation (D. Lgs. n. 152/06) set limits to the concentration of PM_{10} and specific priority pollutants in the atmosphere, and an air quality monitoring system is implemented by Regional Agencies for Environmental Prevention and Protection (ARPA). Nonetheless, several contaminants are not determined despite their potential negative effects on the ecosystem and/or human health.

Traffic pollution is one of the major contributors to the worsening of air quality, particularly in urban areas, hence understanding how traffic pollution markers can distribute in the environment is of utmost importance. Benzothiazoles (BTHs) are tyre-derived particles often used as markers for traffic pollution based on their high detection frequencies in road runoff [\(Asheim et al., 2019](#page-5-0); [Feltracco et al., 2023](#page-5-0); [Maurer et al.,](#page-6-0) [2023\)](#page-6-0). BTHs are a class of heterocyclic aromatic compounds whose main skeleton is formed by a 1,3-thiazole ring fused to a benzene ring. Due to their extensive use in a wide range of industrial and consumer products, they are listed as high production volume chemicals [\(Liao et al., 2018](#page-6-0)). They are mainly used as vulcanization accelerators in rubber manufacturing, but also as fungicides in leather and paper production, corrosion inhibitors in antifreeze formulations, pesticides and ultraviolet light stabilizers in textiles and plastics ([Kloepfer et al., 2004](#page-6-0); [Liao](#page-6-0) [et al., 2018](#page-6-0); [Ni et al., 2008\)](#page-6-0). Some BTHs have been used as precursors for pharmaceuticals as they exhibit different kind of biological activities ([Asiri et al., 2020;](#page-5-0) [Chander Sharma et al., 2020](#page-5-0); [Gill et al., 2015](#page-6-0); [Keri](#page-6-0) [et al., 2015](#page-6-0)). BTHs can also have natural sources, as they are constituents of tea leaves and tobacco ([De Wever and Verachtert, 1997;](#page-5-0) [Seo](#page-6-0) [et al., 2000\)](#page-6-0).

According to several studies, BTHs exhibit cytotoxic, mutagenic and carcinogenic properties in microorganisms and humans [\(Ginsberg et al.,](#page-6-0) [2011;](#page-6-0) [Sorahan, 2008](#page-6-0); [Ye et al., 2014](#page-6-0)). They can cause dermal sensitization and respiratory tract irritation [\(Ginsberg et al., 2011](#page-6-0)), and four of them (benzothiazole, 2-hydroxy-benzothiazole, 2-aminobenzothiazole, 2-methylthiobenzothiazole) are reported to bioaccumulate in human adipose tissue ([Wang et al., 2015\)](#page-6-0). In vitro and in vivo assays have demonstrated endocrine disruption linked to BTHs ([Hornung et al.,](#page-6-0) [2015\)](#page-6-0). Studies have also shown high acute toxicity of 2-thiocyanate-methyl-thiobenzothiazole and its transformation products in aquatic organisms [\(MacKinnon and Farrell, 1992](#page-6-0); [Nawrocki et al., 2005](#page-6-0)).

Their growing production in the past years led to an increased release of BTHs in the environment ([Liao et al., 2021](#page-6-0)). In fact, their presence has been reported in wastewater and other receiving water bodies ([Asimakopoulos et al., 2013a;](#page-5-0) [Kloepfer et al., 2005;](#page-6-0) [Matamoros et al.,](#page-6-0) [2010](#page-6-0); [Ni et al., 2008\)](#page-6-0) – as they are not completely removed by wastewater treating plants – but also in sludge ([Karthikraj and Kannan, 2017\)](#page-6-0), sediment [\(Dsikowitzky et al., 2014](#page-5-0); [Spies et al., 1987](#page-6-0)), soil [\(Speltini et al.,](#page-6-0) [2016](#page-6-0)), indoor dust ([Wang et al., 2013](#page-6-0)), indoor [\(Wan et al., 2016\)](#page-6-0) and outdoor air [\(Franklin et al., 2021; Liao et al., 2021\)](#page-6-0), and background snow ([Maurer et al., 2023\)](#page-6-0). Different studies have reported the presence of BTHs in human urine [\(Asimakopoulos et al., 2013b](#page-5-0); [Wang et al., 2015](#page-6-0)).

BTHs are also linked to plastic pollution as they are used as additives. In fact, they have been found in plastic leachate ([Gunaalan et al., 2020](#page-6-0)), which can represent a further pathway of diffusion in the environment. Moreover, BTHs have been determined in clothing textiles [\(Avagyan](#page-5-0) [et al., 2015;](#page-5-0) [Liu et al., 2017](#page-6-0)), suggesting that clothes can potentially be a source of BTHs release into the environment and of dermal exposure to these contaminants.

Studies on the presence of BTHs in environmental matrices such as air particulate matter are scarce. BTH, BTH-SH, BTH-Me, BTH-MeS, BTH-NH2 and BTH-OH were found in urban aerosol in different loca-tions [\(Avagyan et al., 2014](#page-5-0); [Liao et al., 2021](#page-6-0); Nuñez [et al., 2020\)](#page-6-0), but few investigations have been carried out on other BTHs and their dimensional distribution across particle-size fractions. Nuñez [et al. \(2020\)](#page-6-0) reports a ∑BTHs mean concentration of 3.65 ng m⁻³ in PM_{coarse} (2.5–10 µm) and 2.60 ng m⁻³ in PM_{2.5} in an urban area in Terragona, Spain. The load of BTHs was also investigated by [Franklin et al. \(2021\)](#page-6-0) in the atmosphere of a coastal marine environment, concluding that their emission in the atmosphere is primarily attributed to anthropogenic sources. The presence of BTHs in atmopsheric aerosol has implications for air quality in both urban and industrial centers, where these compounds are more concentrated. BTHs seem to be potential contributors to secondary aerosol formation in coastal regions and to play a role in atmopsheric sulphur chemistry ([Franklin et al., 2021\)](#page-6-0). Current research is focusing more and more on emerging contaminants, but there are still shorcomings regarding the occurrence, distribution and behavior of BTHs in atmospheric aerosols.

The aim of the study is for the first time to characterize the particle size distribution of eight BTHs in aerosol collected in the urban area of Venice. This area is located in the Po Valley, which is considered the worst area in Europe for air quality due to its unfavorable geophsysical and micoclimatic characteristics, which prevents an adequate air recycling determining low dispersion of natural and anthropogenic emissions ([Maranzano, 2022](#page-6-0)). The compounds investigated are benzothiazole (BTH), 2-hydroxy-benzothiazole (BTH-OH), 2-aminobenzothiazole (BTH-NH2), 2-methylbenzothiazole (BTH-Me), 2-methylthiobenzothiazole (BTH-MeS), 2-mercaptobenzothiazole (BTH-SH), 2-thiocyanate methyl thiobenzothiazole (BTH-SCNMeS) and benzo-d-thiazole sulfonic acid (BTH-SO₃H). Analyzing the distribution of BTHs across different particle-size fractions is essential for future assessments of environmental risk and human exposure, as particles' properties such as size have a major effect on contaminants' behavior and bioavailability in the environment ([Kim et al., 2015](#page-6-0)). The extensive usage of BTHs implies that they will likely be an environmental issue in the future, considering also the fact that this class of compounds poses growing concerns regarding ecosystems and publich health. Hence, research should focus on a comprehensive study of their occurrence and fate in different environmental matrices, as to improve knowledge on their behavior and better assess their efficiency as markers of tyre wear particles.

2. Material and methods

2.1. Aerosol sampling

Aerosol samples were collected at the Scientific Campus of Ca' Foscari University (45◦28′47″N, 12◦15′12″E, Mestre-Venice, Italy) from August to October 2023, using the 110NR MOUDI™ cascade impactor, which allows to segregate particles of different sizes in eleven stages

with cut-off at 18 μm (S1), 10 μm (S2), 5.6 μm (S3), 3.2 μm (S4), 1.8 μm (S5), 1.0 μm (S6), 0.56 μm (S7), 0.32 μm (S8), 0.18 μm (S9), 0.10 μm (S10) and 0.056 μm (S11). A final back-up filter was used to collect particles with D *<* 0.056 μm (S12). The sampler was placed on the rooftop of a 35 m tall building, as to obtain data representative for the aerosol mixing state and not directly influenced by ground level shortrange sources of pollution such as brake wear, tyre wear and the resuspension of particles by local traffic-produced turbulence.

The impaction plates were made using aluminum foils cut with a hollow cutter to create a 11 μm thick aluminum substrate with a diameter of 47 mm. The back-up filter is made of quartz fiber and was purchased from Filter-Lab (Filtros Anoia, Barcelona, Spain). Aluminum plates were decontaminated with methanol, while the quartz fiber filter (QFF) was decontaminated by a 4h pre-combustion at 400 $^{\circ}$ C in a muffle furnace.

The sampling period for each sample varied from 159 to 242 h, with a total average air volume of 358.6 $m³$ per sample (Table S1). Two field blanks were taken at the beginning and during the sampling period by leaving aluminum disks and quartz filter for few minutes in the sampler, with the air pump turned off.

2.2. Sample treatment

Reagent, standard solutions and materials are reported in Supplementing Material. After sample collection, the filters were stored at − 20 ◦C. Each substrate was weighted using a Ohaus® Pioneer™ analytical balance $(\pm 0.1 \text{ mg})$ before and after sampling, to determine the aerosol mass collected.

All operations of sample treatment were carried out under a laminar flow bench and all rubber-related materials were avoided to minimize contamination, . Each filter was placed in a 15 mL vial, previously decontaminated with methanol, and spiked with 100 ng of isotopically labelled d4-benzothiazole (BTH-D4) as internal standard. The extraction was performed with 10 mL of ultrapure water into a cold ultrasonic bath for 30 min. The extract solution was filtrated using 0.45 μm PTFE filters to remove all particulate and filter traces before instrumental analysis.

2.3. Instrumental analysis

The analytical determination of BTHs in aerosol samples was achieved following the instrumental method recently developed by [Fel](#page-5-0)[tracco et al., \(2023\).](#page-5-0) Briefly, an Ultimate 3000 UHPLC system was coupled with a TSQ Altis™ Plus Triple Quadrupole Mass Spectrometer (Thermo Scientific™, Waltham, USA), equipped with a heated electrospray source (H-ESI) operating both in negative and positive modes.

Chromatographic separation was performed through a Betasil™ C18 column (100 \times 2.1 I.D. mm, 5 µm of particle size) equipped with a guard column Betasil™ Javelin guard C18 (10 \times 2.1 mm, 5 µm) (Thermo Scientific™). Elution was performed using ultrapure water with 0.005% of formic acid as eluent A and MeOH as eluent B. The binary gradient elution program with flow rate of 0.25 mL min⁻¹ was as follows: 0–3 min isocratic step at 5% eluent B; 3–5 min gradient from 5 to 45%; 5–8 isocratic step at 45%; 8–19 gradient from 45 to 100%; 19–24 isocratic washing step at 100%; and 24–28 equilibration stage at 5% eluent B. Injection volume was 100 μL.

The mass spectrometer's source parameters were set as follows: H-ESI ion source type, static spray voltage, 2700 V positive ion spray voltage, − 2300 V negative ion spray voltage, sheath gas 40 Arb, auxiliary gas 10 Arb, sweep gas 0 Arb, ion transfer tube temperature 200 ◦C, and vaporizer temperature 400 ◦C.

2.4. Quality control

To the best of our knowledge, no previous studies have investigated all the selected BTHs (Table S3) in aerosols divided by twelve different particle-size fractions. Quality control was performed by comparing the

peak area of the native compounds with that of the internal standard BTH-D4. To account for instrumental response fluctuations, concentrations were corrected with a response factor calculated by analysing a standard solution with a mean concentration of 10 ng mL⁻¹ of native BTHs and 10 ng mL^{-1} of BTH-D4.

Blanks, MQL, MDL, trueness, recovery and precision were calculated for both aluminum and quartz fiber substrates by analysing a filter spiked with 100 ng of native BTHs. MDL and MQL were calculated as 3 and 10 time the standard deviation of the mean blank value, respectively. Trueness was calculated by dividing the difference between the quantified value (Q) and the true valute (T) by the true value: $(Q - T)/T$. Precision is expressed as the relative percentual standard deviation, also known as coefficient of variation (CV%). A summary of all validation parameters is reported in Supplementary Material (Table S4).

3. Results and discussion

3.1. Total concentration and abundances of BTHs

All target compounds were present in the samples analyzed in this study. The total concentration of BTHs ([∑]BTHs) in aerosol, calculated as the sum of their twelve size distributions in all samples, ranged from 0.4 to 2.7 ng m⁻³, with a mean value of 1.1 \pm 0.7 ng m⁻³. Samples collected during the summer period show the highest mean concentrations, with a ∑BTHs mean concentration almost twice as high as those collected during the early autumn weeks (Table S5). As shown in Fig. 1, the predominant compounds are BTH-SH and BTH (which represents respectively 30% and 28% of the total BTHs content, both with an average concentration of 0.3 \pm 0.3 ng m^{-3}), followed by BTH-SO₃H and BTH-MeS (both 17%, 0.19 \pm 0.05 and 0.19 \pm 0.13 ng m⁻³ respectively), BTH-OH (8%, 0.09 \pm 0.06 ng m⁻³) and BTH-Me (1%, 5.6 \pm 6.3 pg m⁻³). BTH-NH2 and BTH-SCNMeS were the less abundant compounds (*<*1%, 2.2 ± 0.6 pg m⁻³ and 1.2 ± 1.3 pg m⁻³ respectively).

3.2. Size-distribution of BTHs in size-segregated aerosol

[Fig. 2](#page-3-0) describes the size distribution of each BTHs in terms of geometric mean aerodynamic diameter (a) and their temporal sizesegregated trend (b). All target compounds were mainly distributed in

Fig. 1. Relative mean abundances of BTHs in Total Suspended Particles (TSP) in atmospheric aerosol collected in the urban aera of Mestre-Venice from August to October 2023. BTH-SCNMeS and BTH-NH2 were not included as they represented *<*1% of the total BTHs content.

Fig. 2. Size distribution of BTHs (a) and their temporal size-segregated concentration (b) in aerosol sampled in the urban aera of Mestre-Venice from August to October 2023.

the finest fractions of aerosol $\left($ <1.8 μ m), apart from BTH-SO₃H which is equally distributed in the coarser and finer fractions. The fine fraction of aerosols is usually defined as the one composed by particles in the range between 0.1 and 2.5 μm; in our case, since the sampler employed did not have a 2.5 μm cut-off, we decided to consider 1.8 μm as the upper limit of the fine mode. The fine fraction of airborne particulate matter is the most concerning regarding the potential to cause harmful effects on human health. In particular, when inhaled, PM particles with diameter *<*2.5 μm are more likely to penetrate the lungs and eventually reach the blood stream, causing significant health problems ([Kim et al., 2015\)](#page-6-0) and potentially act an exposure path to $PM_{2.5}$ -bound pollutants (Sánchez-Piñero [et al., 2022\)](#page-6-0). Exposure to the fine air particulate matter and traffic-related air pollution has been associated with enhanced mortality, cardiovascular and respiratory diseases and allergic reactions (Marconi, 2003; Pöschl, 2005). The fact that BTHs in our samples tend to accumulate in $PM_{1.8}$ is in contrast to what was found by Nuñez et al. [\(2020\),](#page-6-0) who observed higher concentrations in particulate matter whose size ranged from 2.5 to 10 μm. We believe this could be due to two reasons: 1) the peculiar orographic characteristics of the Po Valley, where our sampling site is located; 2) the fact that we chose to sample at 35 m a.g.l, obtaining data more representative for the urban boundary layer and less influenced by ground level emission sources and resuspension phenomenon. In the following paragraphs we aim to provide a detailed explanation for both reasons.

The surrounding orography of the Po Valley, which is enclosed on three sides by mountain ranges (Alps and Apennines), influences the meteorological conditions and determines a regional climate characterized by low wind regimes, especially in winter, and the onset of thermal inversion conditions. This prevents atmospheric dispersion and air masses exchange and can create situations where the upward movement of air from underlying layers is hindered, thereby reducing the vertical dispersion of atmospheric aerosol ([Maranzano, 2022](#page-6-0); [Speranza and Caggiano, 2023\)](#page-6-0). Due to these mechanisms, fine aerosol particles tend to persist in the atmosphere. Moreover, thermal inversion can cause high humidity conditions and lead to an increase in the fine size fraction of aerosols [\(Speranza and Caggiano, 2023](#page-6-0)).

Furthermore, the height of our sampling location is to be considered. Previous studies [\(Brines et al., 2016](#page-5-0); [Chan and Kwok, 2000](#page-5-0)) show variations in the vertical particle-size distribution profile of aerosols in urban settings, with street level aerosols generally enriched in coarser particles due to the presence of the emission sources (e.g. tyre wear, brake wear). Rooftop level pollution, which is more reflective of the urban background layer, is mainly influenced by meteorological and transport situations, and less by the direct emissions sources (Schäfer et al., 2006).

We calculated PM mass concentrations for each dimensional class for each of our samples (Table S_6). All samples, except two (1st – 11th Aug and 18th – 25th Sep), show a higher PM mass concentration in the fraction composed by particles with diameter *<*1.8 μm. Suspended particles greater in size are more affected by gravity and thus have a shorter residence time in air, leaving only smaller particles to diffuse towards upper levels ([Chan and Kwok, 2000](#page-5-0)). This could further explain why BTHs in our samples predominantly distribute in the fine fraction of aerosol. It implies that the aerosol composition at rooftop level is mainly influenced by atmospheric transport and processes, rather than by the direct contribution of nearby ground level sources. This finding suggests that further studies are necessary on the vertical distribution patterns of traffic-emitted pollutants, as assessing their vertical profiles in urban settings could aid in discriminating their sources and understanding their behaviour.

BTH, BTH-Me, BTH-MeS, BTH-SH and BTH-OH show similar trend and size distribution ($Fig. 2$). The majority of samples present a monomodal trend, with maxima centered between 0.2 and 1 μm; samples corresponding to 21st – 31st August and 11th – 18th September show a bimodal distribution instead, with maxima centered at 0.5 and 6 μm and at 1 and 10 μm, respectively. The aerodynamic diameter of aerosol particles is a factor that contributes to determining their residence time in the atmosphere and their physical and chemical properties ([Prospero](#page-6-0) [et al., 1983;](#page-6-0) [Seinfeld and Pandis, 2016\)](#page-6-0). A similar size distribution suggests similar sources and environmental fate. It's interesting to note that BTH, BTH-MeS, BTH-SH and BTH-OH all present the highest concentration in the sampling period from 11th September to 18th September, with an enrichment in the coarse fraction compared to other samples, further implying a common origin.

The concentrations of BTH-SH and BTH are consistent with those found by [Avagyan et al. \(2014\)](#page-5-0) in urban air at Hornsgatan in Stockholm. BTH-SH is the main compound used in vulcanizing accelerators in rubber manufacture, suggesting tyre debris as its main source. It has shown potential mutagenic effects [\(Haroune et al., 2004\)](#page-6-0) and a study found a significant increase of the incidence of cancer on production workers exposed to BTH-SH [\(Sorahan, 2008\)](#page-6-0). The high relative concentration of BTH-SH could imply that human exposure might be greater than previously assumed and not limited to occupational exposure.

BTH-NH2 shows a variable size distribution [\(Fig. 2](#page-3-0)a), ranging from monomodal to trimodal depending on the sampling period, with maxima mainly laying on the fine and ultrafine regions.

BTH-SO₃H presents a bimodal size distribution ($Fig. 2a$ $Fig. 2a$), with maxima centered in the coarse fraction. Its different distribution compared to the other BTHs suggests a different source. BTH-SO₃H was found to be the most concentrated compound in road dust [\(Feltracco et al., 2023\)](#page-5-0) and in municipal wastewater [\(Kloepfer et al., 2004](#page-6-0)), which could represent two major local sources of BTH-SO3H in the atmosphere. While the nucleation and the accumulation mode can derive, respectively, from the nucleation of super-saturated vapours and from coagulation of existing particles or gas-to-particle conversion, coarse particles tend to derive from resuspension and erosion phenomena. Being our sampling site an urban area with low surfaces potentially subject to erosion, resuspension is the most likely emission process for coarse particles. This further support the hypothesis of resuspension of road dust as an important source of BTH-SO₃H in the atmosphere. However, literature on the presence of BTH-SO₃H in the air is scarce and further research is necessary to determine its sources and behavior in the particulate phase of aerosols.

BTH-SCNMeS has the lowest concentration compared to the other target compounds, and is absent in samples corresponding to 11th – 21st August and 9th October – 16th October ([Fig. 2b](#page-3-0)). Its size distribution is bimodal, with higher maxima in the fine fraction ([Fig. 2a](#page-3-0)). BTH-SCNMeS is a biocide used in leather, paper and water-treatment industries and it is characterized by high acute toxicity for aquatic organisms ([Nawrocki](#page-6-0) [et al., 2005](#page-6-0)). However, photolysis due to sunlight is efficient in degrading BTH-SCNMeS into less toxic products ([Bertoldi et al., 2020](#page-5-0)); this could explain its scarse concentration in the analyzed samples.

3.3. Diagnostic ratios of BTHs and their temporal trend

BTH-SH photodegrades into BTH-SO₃H, while BTH photodegrades into BTH-OH (Zajíčková and Párkányi, 2008). The ratios between BTH-SO3H/BTH-SH and BTH-OH/BTH can be indicative of the aerosol's state of oxidation. We calculated these ratios for the coarse, fine and ultrafine fractions for each sample (Table S7) and plotted their temporal trend [\(Fig. 3](#page-5-0)). Both BTH-SO₃H/BTH-SH and BTH-OH/BTH values present a spike corresponding to 25th September – 2nd October, particularly evident in the ultrafine fraction. Another spike in the coarse fraction is visible in the sampling period from 11th to 21st August (BTH and BTH-SH concentration in the ultrafine fractions were below MQL therefore the ratio could not be calculated for this specific sampling period). This could carry the evidence of intense oxidative conditions, which might have enhanced photochemical processes leading to an enrichment of BTH-SO₃H and BTH-OH relatively to BTH-SH and BTH respectively. We could not find literature values of these ratios to compare ours with; more extensive research would be beneficial to assess their applicability as markers for photochemical aging processes of organic aerosols.

4. Conclusions

Being high production volume chemicals having a wide range of industrial applications, BTHs are being released in the environment at an increasing rate. Despite being often investigated in urban wastewater, most of the target compounds are not considered due to low concentrations in environmental matrices, and the literature on their presence in other matrices such as airborne particulate matter is limited. The present study provides for the first time a basis for investigation of a broad class of BTHs in aerosol representative of the urban boundary

Fig. 3. Temporal trend of BTH-SO3H/BTH-SH and BTH-OH/BTH ratios in the coarse, fine and ultrafine fraction of aerosol collected at Mestre-Venice during our sampling period.

layer and of their distribution across different particle-size fractions. All target compounds were present in our samples, with concentrations ranging from pg m⁻³ to ng m⁻³. The dimensional distribution indicates an enrichment of all BTHs in the finest fraction of aerosol, probably due to two reasons: 1) the peculiar orographic characteristics of the Po Valley, which prevents air masses exchange thereby leading to an increase in the fine size fraction of aerosols; 2) the fact that by choosing to sample at 35 m a.g.l we obtained data more reflective of the aerosol mixing state and less influenced by direct emission sources located at ground level, which generally determine an enrichment in coarser particles. $BTH-SO₃H$ is the only compound which present a different size distribution compared to the other BTHs, suggesting a different source. The highest relative abundance of BTH-SH was not surprising, since it is the main vulcanizing agent used in rubber manufacturing; this however suggests that human exposure to its mutagenic properties may be underestimated.

This study provides valuable data on the presence of BTHs in urban size-segregated aerosol that will help future research on the sources, pathways, and fate of these compounds in the environment. More samples should be considered to monitor their seasonal trend and their vertical distribution in airborne particulate matter, since there could be differences in their dimensional distribution between street and rooftop level.

CRediT authorship contribution statement

Eleonora Favaro: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation. **Giovanna Mazzi:** Writing – review & editing, Methodology, Formal analysis, Conceptualization. **Elena Barbaro:** Writing – review & editing. **Mauro Masiol:** Writing – review & editing. **Agata Alterio:** Writing – review & editing, Methodology, Formal analysis. **Andrea Gambaro:** Writing – review & editing, Supervision, Conceptualization. **Matteo Feltracco:** Writing – review & editing, Supervision, Conceptualization.

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.](https://doi.org/10.1016/j.atmosenv.2024.120784) [org/10.1016/j.atmosenv.2024.120784.](https://doi.org/10.1016/j.atmosenv.2024.120784)

References

- Asheim, J., Vike-Jonas, K., Gonzalez, S.V., Lierhagen, S., Venkatraman, V., Veivåg, I.-L. S., Snilsberg, B., Flaten, T.P., Asimakopoulos, A.G., 2019. Benzotriazoles, benzothiazoles and trace elements in an urban road setting in Trondheim, Norway: Re-visiting the chemical markers of traffic pollution. Sci. Total Environ. 649, 703–711. [https://doi.org/10.1016/j.scitotenv.2018.08.299.](https://doi.org/10.1016/j.scitotenv.2018.08.299)
- Asimakopoulos, A.G., Ajibola, A., Kannan, K., Thomaidis, N.S., 2013a. Occurrence and removal efficiencies of benzotriazoles and benzothiazoles in a wastewater treatment plant in Greece. Sci. Total Environ. 452–453, 163–171. [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.scitotenv.2013.02.041) [scitotenv.2013.02.041.](https://doi.org/10.1016/j.scitotenv.2013.02.041)
- Asimakopoulos, A.G., Wang, L., Thomaidis, N.S., Kannan, K., 2013b. Benzotriazoles and benzothiazoles in human urine from several countries: a perspective on occurrence, biotransformation, and human exposure. Environ. Int. 59, 274–281. [https://doi.org/](https://doi.org/10.1016/j.envint.2013.06.007) [10.1016/j.envint.2013.06.007](https://doi.org/10.1016/j.envint.2013.06.007).
- Asiri, Y.I., Alsayari, A., Muhsinah, A.B., Mabkhot, Y.N., Hassan, M.Z., 2020. Benzothiazoles as potential antiviral agents. J. Pharm. Pharmacol. 72, 1459–1480. [https://doi.org/10.1111/jphp.13331.](https://doi.org/10.1111/jphp.13331)
- Avagyan, R., Luongo, G., Thorsén, G., Östman, C., 2015. Benzothiazole, benzotriazole, and their derivates in clothing textiles—a potential source of environmental pollutants and human exposure. Environ. Sci. Pollut. Res. 22, 5842–5849. [https://](https://doi.org/10.1007/s11356-014-3691-0) [doi.org/10.1007/s11356-014-3691-0.](https://doi.org/10.1007/s11356-014-3691-0)
- Avagyan, R., Sadiktsis, I., Bergvall, C., Westerholm, R., 2014. Tire tread wear particles in ambient air—a previously unknown source of human exposure to the biocide 2 mercaptobenzothiazole. Environ. Sci. Pollut. Res. 21, 11580–11586. [https://doi.org/](https://doi.org/10.1007/s11356-014-3131-1) [10.1007/s11356-014-3131-1](https://doi.org/10.1007/s11356-014-3131-1).
- Bertoldi, C., De Cássia Campos Pena, A., Dallegrave, A., Fernandes, A.N., Gutterres, M., 2020. Photodegradation of emerging contaminant 2-(tiocyanomethylthio) benzothiazole (TCMTB) in aqueous solution: Kinetics and transformation products. Bull. Environ. Contam. Toxicol. 105, 433–439. [https://doi.org/10.1007/s00128-](https://doi.org/10.1007/s00128-020-02954-2) [020-02954-2.](https://doi.org/10.1007/s00128-020-02954-2)
- Brines, M., Dall'Osto, M., Amato, F., Cruz Minguillón, M., Karanasiou, A., Alastuey, A., Querol, X., 2016. Vertical and horizontal variability of $PM₁₀$ source contributions in Barcelona during SAPUSS. Atmospheric Chem. Phys. 16, 6785–6804. [https://doi.](https://doi.org/10.5194/acp-16-6785-2016) [org/10.5194/acp-16-6785-2016](https://doi.org/10.5194/acp-16-6785-2016).
- Chan, L.Y., Kwok, W.S., 2000. Vertical dispersion of suspended particulates in urban area of Hong Kong. Atmos. Environ. 34, 4403–4412. [https://doi.org/10.1016/S1352-](https://doi.org/10.1016/S1352-2310(00)00181-3) [2310\(00\)00181-3](https://doi.org/10.1016/S1352-2310(00)00181-3).
- Chander Sharma, P., Sharma, D., Sharma, A., Bansal, K.K., Rajak, H., Sharma, S., Thakur, V.K., 2020. New horizons in benzothiazole scaffold for cancer therapy: advances in bioactivity, functionality, and chemistry. Appl. Mater. Today 20, 100783. <https://doi.org/10.1016/j.apmt.2020.100783>.
- De Wever, H., Verachtert, H., 1997. Biodegradation and toxicity of benzothiazoles. Water Res. 31, 2673–2684. [https://doi.org/10.1016/S0043-1354\(97\)00138-3.](https://doi.org/10.1016/S0043-1354(97)00138-3)
- Dsikowitzky, L., Nordhaus, I., Sujatha, C.H., Akhil, P.S., Soman, K., Schwarzbauer, J., 2014. A combined chemical and biological assessment of industrial contamination in an estuarine system in Kerala, India. Sci. Total Environ. 485–486, 348–362. [https://](https://doi.org/10.1016/j.scitotenv.2014.03.034) [doi.org/10.1016/j.scitotenv.2014.03.034.](https://doi.org/10.1016/j.scitotenv.2014.03.034)
- Feltracco, M., Mazzi, G., Barbaro, E., Rosso, B., Sambo, F., Biondi, S., Barbante, C., Gambaro, A., 2023. Occurrence and phase distribution of benzothiazoles in

untreated highway stormwater runoff and road dust. Environ. Sci. Pollut. Res. 30, 107878–107886. <https://doi.org/10.1007/s11356-023-30019-4>.

- Franklin, E.B., Alves, M.R., Moore, A.N., Kilgour, D.B., Novak, G.A., Mayer, K., Sauer, J. S., Weber, R.J., Dang, D., Winter, M., Lee, C., Cappa, C.D., Bertram, T.H., Prather, K. A., Grassian, V.H., Goldstein, A.H., 2021. Atmospheric benzothiazoles in a coastal marine environment. Environ. Sci. Technol. 55, 15705–15714. https://doi.org/
10.1021/acs.est.1c04422. est.1c04422.
- Gill, R.K., Rawal, R.K., Bariwal, J., 2015. Recent advances in the chemistry and biology of benzothiazoles. Arch. Pharm. (Weinheim) 348, 155–178. [https://doi.org/](https://doi.org/10.1002/ardp.201400340) [10.1002/ardp.201400340.](https://doi.org/10.1002/ardp.201400340)
- Ginsberg, G., Toal, B., Kurland, T., 2011. Benzothiazole toxicity assessment in support of synthetic turf field human health risk assessment. J. Toxicol. Environ. Health 74, 1175–1183.<https://doi.org/10.1080/15287394.2011.586943>.
- Gunaalan, K., Fabbri, E., Capolupo, M., 2020. The hidden threat of plastic leachates: A critical review on their impacts on aquatic organisms. Water Res. 184, 116170. [http](https://doi.org/10.1016/j.watres.2020.11617) [s://doi.org/10.1016/j.watres.2020.11617.](https://doi.org/10.1016/j.watres.2020.11617)
- Haroune, N., Combourieu, B., Besse, P., Sancelme, M., Kloepfer, A., Reemtsma, T., De Wever, H., Delort, A.-M., 2004. Metabolism of 2-mercaptobenzothiazole by *Rhodococcus rhodochrous*. Appl. Environ. Microbiol. 70, 6315–6319. [https://doi.org/](https://doi.org/10.1128/AEM.70.10.6315-6319.2004) [10.1128/AEM.70.10.6315-6319.2004](https://doi.org/10.1128/AEM.70.10.6315-6319.2004).
- Hornung, M.W., Kosian, P.A., Haselman, J.T., Korte, J.J., Challis, K., Macherla, C., Nevalainen, E., Degitz, S.J., 2015. *In vitro* , *ex vivo* , and *in vivo* determination of thyroid hormone modulating activity of benzothiazoles. Toxicol. Sci. 146, 254–264. <https://doi.org/10.1093/toxsci/kfv090>.
- Karthikraj, R., Kannan, K., 2017. Mass loading and removal of benzotriazoles, benzothiazoles, benzophenones, and bisphenols in Indian sewage treatment plants. Chemosphere 181, 216-223. https://doi.org/10.1016/j.chemosphere.2017.04.
- Keri, R.S., Patil, M.R., Patil, S.A., Budagumpi, S., 2015. A comprehensive review in current developments of benzothiazole-based molecules in medicinal chemistry. Eur. J. Med. Chem. 89, 207–251. [https://doi.org/10.1016/j.ejmech.2014.10.059.](https://doi.org/10.1016/j.ejmech.2014.10.059)
- Kim, K.-H., Kabir, E., Kabir, S., 2015. A review on the human health impact of airborne particulate matter. Environ. Int. 74, 136–143. [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.envint.2014.10.005) [envint.2014.10.005](https://doi.org/10.1016/j.envint.2014.10.005).
- Kloepfer, A., Gnirss, R., Jekel, M., Reemtsma, T., 2004. Occurrence of benzothiazoles in municipal wastewater and their fate in biological treatment. Water Sci. Technol. 50, 203–208. [https://doi.org/10.2166/wst.2004.0329.](https://doi.org/10.2166/wst.2004.0329)
- Kloepfer, A., Jekel, M., Reemtsma, T., 2005. Occurrence, sources, and fate of benzothiazoles in municipal wastewater treatment plants. Environ. Sci. Technol. 39, 3792–3798.<https://doi.org/10.1021/es048141e>.
- Liao, C., Kim, U.-J., Kannan, K., 2018. A review of environmental occurrence, fate, exposure, and toxicity of benzothiazoles. Environ. Sci. Technol. 52, 5007–5026. [https://doi.org/10.1021/acs.est.7b05493.](https://doi.org/10.1021/acs.est.7b05493)
- Liao, X., Zou, T., Chen, M., Song, Y., Yang, C., Qiu, B., Chen, Z.-F., Tsang, S.Y., Qi, Z., Cai, Z., 2021. Contamination profiles and health impact of benzothiazole and its derivatives in PM2.5 in typical Chinese cities. Sci. Total Environ. 755, 142617 [https://doi.org/10.1016/j.scitotenv.2020.142617.](https://doi.org/10.1016/j.scitotenv.2020.142617)
- Liu, W., Xue, J., Kannan, K., 2017. Occurrence of and exposure to benzothiazoles and benzotriazoles from textiles and infant clothing. Sci. Total Environ. 592, 91–96. <https://doi.org/10.1016/j.scitotenv.2017.03.090>.
- MacKinnon, D.L., Farrell, A.P., 1992. The effect of 2-(*Thiocyanomethylthio*)benzothiazole on juvenile coho salmon (*Oncorhynchus Kisutch*): sublethal toxicity testing. Environ. Toxicol. Chem. 11, 1541–1548.<https://doi.org/10.1002/etc.5620111104>.
- Maranzano, P., 2022. Air quality in lombardy, Italy: an overview of the environmental monitoring system of ARPA lombardia. Earth 3, 172–203. [https://doi.org/10.3390/](https://doi.org/10.3390/earth3010013) [earth3010013](https://doi.org/10.3390/earth3010013).
- [Marconi, A., 2003. Materiale particellare aerodisperso: definizioni, effetti sanitari,](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref29) [misura e sintesi delle indagini ambientali effettuate a Roma. Ann. DellIstituto Super.](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref29) Sanità [39, 329](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref29)-342.
- Matamoros, V., Jover, E., Bayona, J.M., 2010. Occurrence and fate of benzothiazoles and benzotriazoles in constructed wetlands. Water Sci. Technol. 61, 191-198. https:/ [doi.org/10.2166/wst.2010.797.](https://doi.org/10.2166/wst.2010.797)
- Maurer, L., Carmona, E., Machate, O., Schulze, T., Krauss, M., Brack, W., 2023. Contamination pattern and risk assessment of polar compounds in snow melt: an

integrative proxy of road runoffs. Environ. Sci. Technol. 57, 4143–4152. [https://doi.](https://doi.org/10.1021/acs.est.2c05784) [org/10.1021/acs.est.2c05784](https://doi.org/10.1021/acs.est.2c05784).

- Nawrocki, S.T., Drake, K.D., Watson, C.F., Foster, G.D., Maier, K.J., 2005. Comparative aquatic toxicity evaluation of 2-(thiocyanomethylthio)benzothiazole and selected degradation products using Ceriodaphnia dubia. Arch. Environ. Contam. Toxicol. 48, 344–350. <https://doi.org/10.1007/s00244-004-0105-1>.
- Ni, H.-G., Lu, F.-H., Luo, X.-L., Tian, H.-Y., Zeng, E.Y., 2008. Occurrence, phase distribution, and mass loadings of benzothiazoles in riverine runoff of the pearl river delta, China. Environ. Sci. Technol. 42, 1892–1897. [https://doi.org/10.1021/](https://doi.org/10.1021/es071871c) [es071871c.](https://doi.org/10.1021/es071871c)
- Nuñez, A., Vallecillos, L., Marcé, R.M., Borrull, F., 2020. Occurrence and risk assessment of benzothiazole, benzotriazole and benzenesulfonamide derivatives in airborne particulate matter from an industrial area in Spain. Sci. Total Environ. 708, 135065 [https://doi.org/10.1016/j.scitotenv.2019.135065.](https://doi.org/10.1016/j.scitotenv.2019.135065)
- Pöschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angew. Chem. Int. Ed. 44, 7520–7540. [https://doi.org/10.1002/](https://doi.org/10.1002/anie.200501122) [anie.200501122.](https://doi.org/10.1002/anie.200501122)
- Prospero, J.M., Charlson, R.J., Mohnen, V., Jaenicke, R., Delany, A.C., Moyers, J., Zoller, W., Rahn, K., 1983. The atmospheric aerosol system: an overview. Rev. Geophys. 21, 1607–1629. [https://doi.org/10.1029/RG021i007p01607.](https://doi.org/10.1029/RG021i007p01607)
- [Spies, Robert B., Andresen, Brian D., Rice Jr., David W., 1987. Benzothiazoles in](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref37) [estuarine sediments as indicators of street runoff. Nature 327, 697](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref37)–699.
- Sánchez-Piñero, J., Novo-Quiza, N., Pernas-Castaño, C., Moreda-Piñeiro, J., Muniategui-Lorenzo, S., López-Mahía, P., 2022. Inhalation bioaccessibility of multi-class organic pollutants associated to atmospheric PM2.5: correlation with PM2.5 properties and health risk assessment. Environ. Pollut. 307, 119577 [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.envpol.2022.119577) [envpol.2022.119577](https://doi.org/10.1016/j.envpol.2022.119577).
- [Seinfeld, J.H., Pandis, Spyros N., 2016. Atmospheric Chemistry and Physics: from Air](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref39) [Pollution to Climate Change, third ed. Wiley.](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref39)
- Seo, K.W., Park, M., Kim, J.G., Kim, T.W., Kim, H.J., 2000. Effects of benzothiazole on the xenobiotic metabolizing enzymes and metabolism of acetaminophen. J. Appl. Toxicol. 20, 427-430. [https://doi.org/10.1002/1099-1263\(200011/12\)20:6](https://doi.org/10.1002/1099-1263(200011/12)20:6<427::AID-JAT707>3.0.CO;2)< [AID-JAT707](https://doi.org/10.1002/1099-1263(200011/12)20:6<427::AID-JAT707>3.0.CO;2)*>*3.0.CO;2.
- Sorahan, T., 2008. Cancer risks in chemical production workers exposed to 2 mercaptobenzothiazole. Occup. Environ. Med. 66, 269–273. [https://doi.org/](https://doi.org/10.1136/oem.2008.041400) [10.1136/oem.2008.041400.](https://doi.org/10.1136/oem.2008.041400)
- Speltini, A., Sturini, M., Maraschi, F., Porta, A., Profumo, A., 2016. Fast low-pressurized microwave-assisted extraction of benzotriazole, benzothiazole and benezenesulfonamide compounds from soil samples. Talanta 147, 322–327. [https://](https://doi.org/10.1016/j.talanta.2015.09.074) doi.org/10.1016/j.talanta.2015.09.074.
- Speranza, A., Caggiano, R., 2023. Meteorological variables and PM10 exceedances effect on aerosol particles in a low emission zone using compositional data analysis. J. Geochem. Explor. 255, 107322 [https://doi.org/10.1016/j.gexplo.2023.107322.](https://doi.org/10.1016/j.gexplo.2023.107322)
- Wan, Y., Xue, J., Kannan, K., 2016. Benzothiazoles in indoor air from Albany, New York, USA, and its implications for inhalation exposure. J. Hazard Mater. 311, 37–42. <https://doi.org/10.1016/j.jhazmat.2016.02.057>.
- Wang, L., Asimakopoulos, A.G., Kannan, K., 2015. Accumulation of 19 environmental phenolic and xenobiotic heterocyclic aromatic compounds in human adipose tissue. Environ. Int. 78, 45–50. [https://doi.org/10.1016/j.envint.2015.02.015.](https://doi.org/10.1016/j.envint.2015.02.015)
- Wang, L., Asimakopoulos, A.G., Moon, H.-B., Nakata, H., Kannan, K., 2013. Benzotriazole, benzothiazole, and benzophenone compounds in indoor dust from the United States and east asian countries. Environ. Sci. Technol. 47, 4752–4759. <https://doi.org/10.1021/es305000d>.
- Yadav, D., Rangabhashiyam, S., Verma, P., Singh, P., Devi, P., Kumar, P., Hussain, C.M., Gaurav, G.K., Kumar, K.S., 2021. Environmental and health impacts of contaminants of emerging concerns: recent treatment challenges and approaches. Chemosphere 272, 129492. [https://doi.org/10.1016/j.chemosphere.2020.129492.](https://doi.org/10.1016/j.chemosphere.2020.129492)
- Ye, Y., Weiwei, J., Na, L., Mei, M., Kaifeng, R., Zijian, W., 2014. Application of the SOS/ umu test and high-content *in vitro* micronucleus test to determine genotoxicity and cytotoxicity of nine benzothiazoles. J. Appl. Toxicol. 34, 1400-1408. https://o [org/10.1002/jat.2972.](https://doi.org/10.1002/jat.2972)
- Zajíčková, Z., Párkányi, C., 2008. Photodegradation of 2-mercaptobenzothiazole [disulfide and related benzothiazoles. Photodegradation 2-mercaptobenzothiazole](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref50) [disulfide relat. Benzothiazoles 45, 303](http://refhub.elsevier.com/S1352-2310(24)00459-X/sref50)–306.