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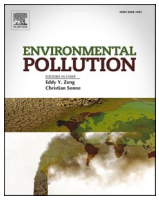

Not so pristine: airborne benzothiazoles and organophosphate flame retardants in an alpine site under anthropogenic stress☆

Eleonora Favaro [a,b], Elena Barbaro [b,a,*], Henri Diémoz [c], Jacopo Gabrieli [b], Fabrizio De Blasi [b], Mara Bortolini [a,d], Andrei Munteanu [a,b], Giulio Cozzi [b,a], Warren R.L. Cairns [b], Carlo Barbante [a,b], Andrea Gambaro [a,b], Matteo Feltracco [a,b]

[a] Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, via Torino 155, 30172, Venice Mestre, VE, Italy
[b] Institute of Polar Sciences, National Research Council (CNR-ISP), via Torino 155, 30172, Venice Mestre, VE), Italy
[c] Atmosphere and Solar Radiation Deparment, Environmental Protection Agency (ARPA) of the Aosta Valley, Saint-Christophe, 11020, Italy
[d] Department of Geosciences, University of Padova, Via G. Gradenigo 6, 35131, Padova, Italy

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ABSTRACT

Although mountainous areas are often regarded as pristine environments due to their remote locations, anthropogenic pollutants can still reach through local emissions or regional atmospheric circulation. This study provides the first assessment of background concentrations of benzothiazoles (BTHs) and organophosphate flame retardants (OPFRs) in PM_{10} at a high-altitude site in the Eastern Italian Alps. Chlorinated OPFRs, particularly TCEP and TCPP, were dominant with concentration levels in the order of ng m^{-3}, comparable to those detected in urban environments and reflecting their increasing application as substitutes for brominated flame retardants. BTH-SO_3H was the most abundant benzothiazole derivative, indicating resuspension of particles originating from tyre wear as a major source. Both classes of target compounds exhibited temporal variations driven by thermally induced upslope winds and mixed-layer dynamics. Multivariate statistical analysis revealed a clear separation of BTHs and OPFRs from biogenic and crustal aerosol constituents, confirming a predominantly anthropogenic origin and highlighting their potential as tracers of human impact in mountain environments.

1. Introduction

High-mountain regions are generally far from urbanized and industrialized areas, where the majority of anthropogenic pollution sources are located, and they are typically considered pristine environments. However, synoptic and regional atmospheric circulation patterns can determine the transport of pollutants from nearby regions. For example, thermally driven winds develop over complex topography following a diurnal cycle and represent a systematic characteristic of mountain weather and climate (Giovannini et al., 2017; Schmidli, 2013; Serafin and Zardi, 2010; Wagner et al., 2015; Zardi and Whiteman, 2013) that determines the regular exchange of air masses between lowlands and uplands. High-altitude remote areas are also subject to long-range transport of air masses potentially carrying contaminants along (Bukowiecki et al., 2016).

The Italian alpine region is of particular interest due to its sensitive environment and its proximity to the Po Valley, a major pollution hotspot in Europe. Here, intense emissions from densely populated areas and industrial and agricultural activities combine with topographic and microclimatic conditions that promote atmospheric stability, preventing air masses exchange and the dispersion of natural and anthropogenic pollution (Bigi and Ghermandi, 2014; Diémoz et al., 2019a, 2019b; Fuzzi et al., 2015; Maranzano, 2022; Speranza and Caggiano, 2023). Pollution in alpine areas can also originate from local tourism (Romeo et al., 2021). In particular, the Dolomites in the Eastern Italian Alps are part of the UNESCO World Heritage and constitute a well-established tourist destination in both winter and summer (Franch et al., 2006).

Italian air quality is monitored by Regional Agencies for

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* Corresponding author. Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, via Torino 155, 30172, Venice Mestre, VE, Italy.

E-mail addresses: eleonora.favaro@unive.it (E. Favaro), elena.barbaro@cnr.it (E. Barbaro), h.diemoz@arpa.vda.it (H. Diémoz), jacopo.gabrieli@cnr.it (J. Gabrieli), fabrizio.deblasi@cnr.it (F. De Blasi), mara.bortolini@unipd.it (M. Bortolini), giulio.cozzi@cnr.it (G. Cozzi), warrenraymondlee.cairns@cnr.it (W.R.L. Cairns), barbante@unive.it (C. Barbante), gambaro@unive.it (A. Gambaro), matteo.feltracco@unive.it (M. Feltracco).

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Environmental Prevention and Protection (ARPA), however several contaminants with potential ecological and health impacts remain unmonitored, and daily mean PM_{10} concentration and the number of exceedance days remain above regulatory thresholds, mainly due to the persistent impact of Po Valley Pollution (SNPA, 2024). Recent literature addresses the growing occurrence of emerging high production volume organic compounds in the atmosphere (Yadav et al., 2021), reinforcing the need for their monitoring. This growing attention extends beyond the identification of novel contaminants to reassessing PM_{10} emission sources, which are undergoing significant changes. The global shift toward vehicle electrification is leading to a reduction in exhaust emissions, while at the same time, changes in human activity patterns, such as the increase in tourism in alpine regions, are introducing new and potentially variable contributions to particulate matter (Amato et al., 2014).

Benzothiazoles (BTHs) are heteroaromatic cyclic compounds formed by the fusion of a benzene ring with a 1,3-thiazole ring and characterized by vast industrial and consumer applications. Their primary use is as vulcanization accelerators in rubber manufacturing (Kloepfer et al., 2005; Liao et al., 2018; Ni et al., 2008) and they are recognized as tracers of traffic-related non-exhaust emissions (Asheim et al., 2019) generated by the combination of brake, tyre and road surface wear. Other applications include their use as corrosion inhibitors in antifreeze formulations, ultraviolet light stabilizers in textiles and plastics, biocides in leather, textile and paper industries, and pharmaceutical precursors (Asiri et al., 2020; Chander Sharma et al., 2020; Kloepfer et al., 2005; Liao et al., 2018; Ni et al., 2008).

Toxicological studies indicate that BTHs pose risks to microorganisms, animals and humans, with effects linked to cytotoxicity, genotoxicity, potential carcinogenicity and endocrine disruption (Ginsberg et al., 2011; He et al., 2011; Hornung et al., 2015; Sorahan, 2008). Documented outcomes in humans include respiratory irritation, dermatitis and skin sensitization (Ginsberg et al., 2011). BTH and three of its derivatives (2-hydroxy-benzothiazole, 2-aminobenzothiazol and 2-methylthiobenzothiazole) have also shown to bioaccumulate in adipose tissue (Wang et al., 2015).

BTHs' production has significantly grown is recent years, driving their widespread release in the environment, where they now appear to be ubiquitous (Liao et al., 2021). Their occurrence has been observed across most environmental matrices, including wastewater (Asimakopoulos et al., 2013; Kloepfer et al., 2005; Xue et al., 2024), freshwater (Dsikowitzky et al., 2014; Fries et al., 2011; Herrero et al., 2013; Kong et al., 2015; Matamoros et al., 2010; Ni et al., 2008) and seawater (Hidalgo-Serrano et al., 2019; Munteanu et al., 2025; Zhao et al., 2024), sludge (Asimakopoulos et al., 2013; Herrero et al., 2013; Karthikraj and Kannan, 2017; Stasinakis et al., 2013), sediment (Dsikowitzky et al., 2014; Spies et al., 1987), soil (Speltini et al., 2016; Zhang et al., 2018), urban runoff (Feltracco et al., 2023; Fuchte et al., 2022), indoor dust (Wang et al., 2013) and air (Wan et al., 2016), road dust (Feltracco et al., 2023; Zhang et al., 2018) and background snow (Maurer et al., 2023). BTH derivatives have been detected in plastic leachates, which represent potential pathways for environmental release (Gunaalan et al., 2020), and clothing textiles, that can act as source of human dermal exposure (Avagyan et al., 2015; Liu et al., 2017).

Regarding the atmospheric compartment, BTH derivatives have been found in indoor (Feltracco et al., 2024), urban (Avagyan et al., 2014; Favaro et al., 2024; Liao et al., 2021; Mazzi et al., 2025; Nuñez et al., 2020) and coastal marine aerosols (Franklin et al., 2021), as well as in remote areas such as the Arctic (Barbaro et al., 2024b). Evidence suggests that their atmospheric emissions are primarily anthropogenic and that they may contribute to secondary aerosol formation and influence atmospheric chemistry (Franklin et al., 2021), yet extensive research on their atmospheric distribution and dynamics is still lacking.

Flame retardants (FRs) are functional additives that are added to combustible materials to reduce flammability and prevent the starting and spreading of fires (Yao et al., 2021). Global FRs consumption amounted at 2.72 million tons in 2022, with brominated flame retardants (BFRs) representing 20 % and phosphorus-based 28 % (BBC Research, 2022). This marks a notable shift from 2008, when phosphorus-based FRs accounted for 11 % and BFRs for 23 % of total consumption (X. Wang et al., 2020). Organophosphate flame retardants (OPFRs) are organophosphate triesters consisting in a central phosphate molecule with heterogeneous substituents that can be grouped into halogenated alkyl-, non-halogenated alkyl- and aryl-OPFRs (Bekele et al., 2021). In addition to their use as FRs, these compounds are employed as plasticizers and antifoaming agents in consumer and industrial products and in construction materials (Marklund et al., 2005a, 2003; Van Der Veen and De Boer, 2012; Wei et al., 2015). OPFRs are also oxidation products of phospites, commonly used as antioxidants in plastics (Liu and Mabury, 2018; Venier et al., 2018).

OPFRs have been marketed as substitutes for BFRs due to their presumed reduced persistence in the environment (Blum et al., 2019), but their environmental safety is now questioned. Being additive FR, OPFRs are not chemically bound to materials and thus can easily leach into the environment during their entire lifecycle (Bekele et al., 2021; Kung et al., 2022). OPFRs – especially chlorinated ones – can persist in water and be subject to long-range transport via waterborne routes (Ma et al., 2017; Sühring et al., 2021). While they are not officially classified as Persistent Organic Pollutants (POPs) under the Stockholm Convention, nor included among the substances listed in the Water Framework Directive (WFD) Watch List, they exhibit properties that are consistent with the emerging concept of Persistent Mobile Organic Compounds (PMOCs) and are being increasingly scrutinized (Reemtsma et al., 2016; Rodgers et al., 2018).

Their extensive application has increased human exposure and associated health risks in recent years (Bekele et al., 2021). Toxicological studies evidenced developmental, neurological, reproductive and endocrine disruptive effects on several organisms including humans (Greaves and Letcher, 2014; Heindel et al., 2017; Schang et al., 2016; Van Der Veen and De Boer, 2012; Yuan et al., 2018). Tris(2-chloroethyl) phosphate, tris(1,3-dichloro-2-propyl) phosphate and tris (1-chloro-2-propyl) phosphate are also considered as potential carcinogenics (Bekele et al., 2021; X. Wang et al., 2020). Studies show that OPFRs can bioaccumulate in aquatic organisms, with limited evidence for biomagnifcation in the aquatic food web (Bekele et al., 2021).

Bekele et al. (2021) and Wang et al. (2020) reviewed OPFRs' occurrence in most environmental compartments worldwide, highlighting their presence in wastewater, surface waters, groundwaters, sludge, soil, sediment, outdoor and indoor air, dust and aquatic biota. Different studies have reported the presence of OPFRs in foodstuff and drinking water (Li et al., 2019) and in different human matrices (Cequier et al., 2015; Ding et al., 2016; Gao et al., 2020; He et al., 2018a, 2018b; Hou et al., 2020; L.-Y. Liu et al., 2016; Qiao et al., 2016; Xu et al., 2019). A comparison of BFRs' concentrations at their peak usage with current OPFRs levels in air and water reveals that the latter have reached higher concentrations in numerous environments ranging from urban areas to remote regions such as the Arctic and Antarctic (Blum et al., 2019; X. Wang et al., 2020).

Most literature on OPFRs' occurrence focuses on indoor and aquatic environments, as these represent the primary pathways of human exposure, whereas their presence in the atmosphere has been far less investigated (X. Wang et al., 2020). Airborne OPFRs have been detected in both particle and gas phase in different urban (Clark et al., 2017; D. Liu et al., 2016; Quintana et al., 2007; Ren et al., 2016; Salamova et al., 2014; Wong et al., 2018; Zhou et al., 2017), suburban (Abdollahi et al., 2017; Naccarato et al., 2018; Shoeib et al., 2014), marine (Möller et al., 2012, 2011; Wolschke et al., 2016) and remote sites (Marklund et al., 2005b; Salamova et al., 2014; Sühring et al., 2021). No studies are available in high-mountain aerosol so far.

The aim of this study is twofold: (1) to provide a new sensitive, fast and robust analytical method for the determination and quantification of six OPFRs in aerosols using an ultra-high-pressure liquid

chromatography system coupled to a triple quadrupole mass spectrometer (UHPLC-MS/MS), and (2) to investigate, for the first time, the occurrence of these compounds and eight BTHs in PM_{10} samples collected at a high-altitude background site in the Eastern Italian Alps, to observe temporal trends and to assess sources and transport processes that contribute to their load in the atmosphere. Monitoring BTHs' and OPFRs' background concentration levels in the atmosphere is essential for future assessment of environmental risks and exposure. Considering that these classes of compounds pose growing concerns regarding ecosystems and public health and will likely gain more relevance due to their extensive use, improving knowledge on their fate and behavior is of utmost importance for future research.

2. Experimental

2.1. Aerosol sampling and processing

Sampling was performed using a Skypost PM_{10} low volume sampler (Tecora™, Monza-Brianza, Italy) equipped with a sequential distribution system of 47 mm diameter quartz fiber filters (QFF, Filter Lab, Barcelona, Spain). All filters were previously decontaminated by a 4 h pre-combustion at 400 °C in a muffle furnace.

Aerosol samples were collected from April to October 2023 at Col Margherita Observatory (MRG), a GAW Regional Station (WI-GOS ID 0-380-0-MRG) located in the Eastern Italian Alps, at an altitude of 2543 m a.s.l. in the middle of the Dolomites (46° 22′ 0.059″ N, 11° 47' 30.911" E) (Fig. S1). MRG is more than 5 km away from the nearest town and distant from major direct atmospheric pollution sources in the Po Valley. Due to its location and altitude, MRG is characterized by few orographic obstructions and its atmospheric composition is related to air masses on a regional scale (Barbaro et al., 2020; Dallo et al., 2021; Vardè et al., 2022). However, as a popular alpine destination, the surrounding area is visited by hikers in summer and skiers in winter, which can contributre to minor local inputs.

Sampling resolution was set at 96 h (i.e. one sample every 4 days), resulting in a total of 49 samples. The sampler was set at a flow rate of 38.3 L min^{-1}, with an average air volume of 331 m^3 per sample. Field blanks were taken at the beginning, during and at the end of the sampling campaign by loading a filter into the sampler for 5 min with the air pump turned off.

After sampling, QFFs were enfolded in clean aluminum foil and stored at −20 °C. Each QFF was weighed using a Ohaus® Pioneer™ analytical balance (±0.1 mg) before and after sampling, to determine the mass of aerosol collected.

Before analysis, each filter was broken up into small pieces with steel tweezers and placed in a 15 mL vial, that had been decontaminated beforehand by sonication in ultrapure water at 25 °C for 30 min. Samples were then spiked with 100 ng of isotopically labelled BTH-D4 and TPP-D15 as internal standards and cold-ultrasonically extracted with 10 mL of ultrapure water at 10 °C for 30 min. The extract solution was filtered through 0.45 μm PTFE filters to remove all particulate and filter traces before instrumental analysis.

All operations of sample treatment were carried out inside an ISO 5 clean room (class 100) under a laminar flow bench, and all rubber-related materials were avoided to minimize contamination. Working under highly controlled conditions is crucial to limit blank levels and allow reliable quantification of compounds at the very low concentrations expected in remote areas.

2.2. Analytical measurements

The target compounds are benzothiazole (BTH), 2-hydroxy-benzothiazole (BTH-OH), 2-aminobenzothiazole (BTH-NH_2), 2-methylbenzothiazole (BTH-Me), 2-methylthiobenzothiazole (BTH-MeS), 2-mercaptobenzothiazole (BTH-SH), 2-thiocyanate-methyl-thiobenzothiazole (BTH-SCNMeS), benzo-d-thiazole sulfonic acid (BTH-SO_3H), triethyl phosphate (TEP), trimethyl phosphate (TMP), triphenyl phosphate (TPP), tris(1-chloro-2-propyl) phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP) and tris(1,3-dichloro-2-propyl) phosphate (TDCP). To better define sources and processes, other chemical tracers for biogenic, crustal and anthropogenic sources were determined, including major inorganic ions, 8 saccharides (arabinose, fructose, galactose, glucose, mannose, ribose, xylose and sucrose), 5 alcohol-sugars (arabitol, erythritol, mannitol, sorbitol and maltitol), 3 anhydrosugars (levoglucosan, mannosan and galactosan), methanesulfonic acid (MSA) and C_2-C_7 carboxylic acids (CAs). Details regarding materials and methods are provided in Supplementary Material.

2.3. Quality control

The instrumental method for the determination of BTHs was previously validated by Feltracco et al. (2023) and the entire analytical procedure for the quantification in aerosol samples was validated by Favaro et al. (2024). Full details are provided in the original publications.

For OPFRs analysis, quality control was performed by comparing the peak area of the native compounds with that of the internal standards TPP-D15. To account for instrumental response fluctuations, concentrations were corrected with a response factor calculated by analyzing a standard solution with a mean concentration of 10 ng mL^{-1} of native OPFRs and 10 ng mL^{-1} of TPP-D15.

The instrumental method was validated by determining linear ranges and instrumental limits of detection (LOD) and quantification (LOQ). Linearity was assessed from 1 ng L^{-1} to 100 μg L^{-1}. According to ICH guidelines (ICH, 2024), LOD and LOQ were calculated based on signal-to-noise ratio (S/N) and determined as the concentrations of analyte corresponding to a S/N of 3:1 and 10:1, respectively. Slope, intercept, R^2, LOD and LOQ values are reported in Supplementary Material (Table S5).

The analytical procedure was validated by analyzing five cleaned QFFs spiked with a solution containing native OPFRs (in an average amount of 130 ng) and by assessing blank values, method detection (MDL) and quantification (MQL) limits, trueness, recovery and precision following the guidelines described by Bliesner (2006) and ICH (2024). MDL and MQL were calculated as respectively 3 and 10 times the standard deviation of the mean blank value. Trueness was calculated by dividing the difference between the quantified value (Q) and the true value (T) by the true value: (Q – T)/T. Precision is expressed as the relative percent standard deviation, also known as coefficient of variation (CV%). A summary of all validation parameters is reported in Supplementary Material (Table S6).

2.4. Statistical multivariate analysis and back trajectories calculation

Statistical analysis was conducted using the packages available in R software (version 4.4.2). The completeness of the dataset was checked by removing all variables that had more than 50 % of missing values and, for variables that presented less missing values, by substituting them using Quantile Regression Imputation of Left-Censored data (QRLIC), performed using R package *imputeLCMD*. This method estimates a truncated distribution based on quantile regression and stochastically imputes the missing values by drawing from it (Lazar et al., 2022; Wei et al., 2018). The cleaned dataset was standardized using z-score normalization and Principal Component Analysis (PCA) was applied to investigate the correlation in a noise-cleared model between the different variables, which included all the target compounds. The number of principal components was selected by comparing the scree plot (Fig. S2) and the percentage of cumulative variance explained (Table S10). The data matrix was then transposed to apply a Hierarchical Cluster Analysis (HCA), using Euclidean distance to compute dissimilarities between variables and the Ward's D2 method as joining rule (Müllner, 2025).

The back-trajectories (BTs) of air masses reaching the sampling site were computed by applying the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion model developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory. We used meteorological data from the Global Data Assimilation System (GDAS) set at 1° resolution to generate 120 h BTs beginning at MRG. BTs were computed with a time step of 4 h (00, 04, 08, 12, 16 and 20 UTC) and the resulting multiple trajectories were mean-clustered aggregated into groups based on the scree-plot analysis of the total spatial variance. The HYSPLIT BTs analysis provided useful insights into the potential areas of origin of the air masses transporting aerosol into the study site.

3. Results and discussion

3.1. Occurrence of BTHs in alpine aerosol

Of all the target compounds, BTH-SO_3H was the most frequently detected with concentrations above MQL in the analyzed samples (98 % of samples), followed by BTH-NH_2 (76 %), BTH-SCNMeS (45 %), BTH-SH and BTH-Me (16 %), BTH-MeS (4 %) and BTH and BTH-OH (2 %) (Fig. 1). The total concentration of BTHs (ΣBTHs), calculated as the sum of their contribution in each sample, ranged from 5 pg m^{-3} to 41 pg m^{-3}, with a median value of 12 ± 8 pg m^{-3}. These values are an order of magnitude lower than those found in urban aerosol in different locations (Favaro et al., 2024; Mazzi et al., 2025; Nuñez et al., 2020). This is consistent with what would be expected for a remote area less impacted by direct anthropogenic pollution sources.

BTH-SO_3H had the highest concentration, with a median value of 5 ± 3 pg m^{-3}. BTH-SO_3H as the most abundant benzothiazole is consistent with Mazzi et al. (2025), who investigated the occurrence of BTHs in multiple monitoring stations located in urbanized areas of the Po Valley, and Feltracco et al. (2023), who analyzed the same compounds in road dust and in both particulate and dissolved phase of stormwater runoff. BTH-SO_3H is one of the major degradation byproducts of BTH-SH through both physico-chemical processes and microbial activity (De Wever and Verachtert, 1997; Fiehn et al., 1998; Zajíčková and Párkányi, 2009, 2008). BTH-SH is a key industrial compound as it serves as precursor for various chemical compounds and is the most widely used as vulcanization accelerator in rubber and rubber products manufacturing (Liao et al., 2018). Vulcanization accelerators are reported to leach from tyre and road wear particles, which act as a source of contaminants in the environment (Foscari et al., 2024). Most of the particles emitted during the tyre wear process tend to initially accumulate alongside roads instead of going airborne (Foscari et al., 2024; Grigoratos and Martini, 2014), and are consequently transported to soils or water bodies through road runoff or wastewater treatment plant effluents (Birch et al., 2020; Magnusson et al., 2016). This could lead to an over-time enrichment of BTH-SO_3H in road dust and in receiving environmental compartments due to the degradation of BTH-SH. In fact, BTH-SO_3H was found to be the most concentrated benzothiazole derivative in both influents and effluents of municipal wastewater treatment plants (Kloepfer et al., 2005, 2004). This implies that the resuspension of particles originally derived from tyre wear, either directly from roadsides and soil or from water bodies, could represent a major source of airborne BTH-SO_3H previously formed from the degradation of BTH-SH through a combination of abiotic and biotic degradation processes.

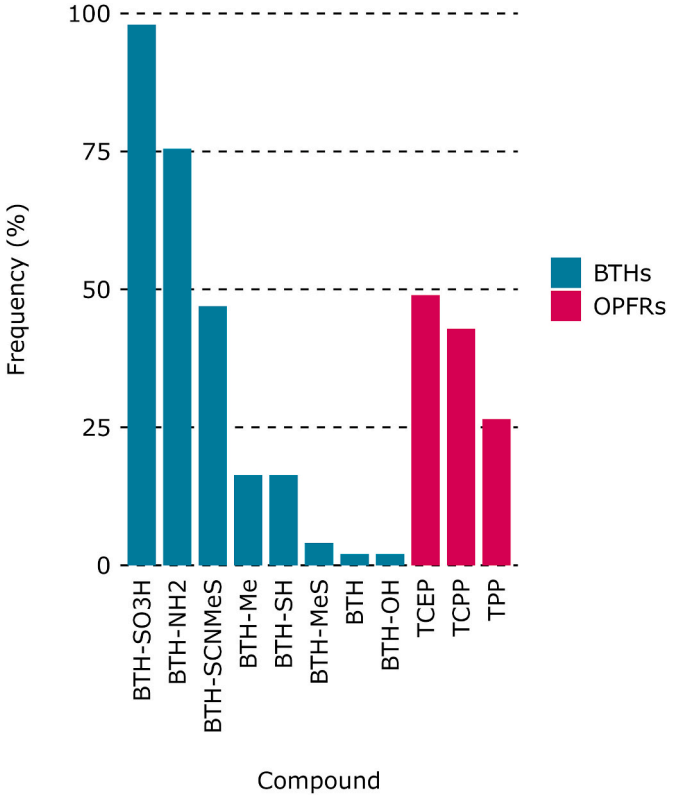

Fig. 1. Detection frequencies of BTHs and OPFRs in PM_{10} at MRG. TMP, TEP and TDCP are not shown here as they were detected in amounts < MQL in all samples.

Additional products of BTH-SH's photodegradation are BTH and, in minor quantity, BTH-Me and BTH-OH, which represent further degradation products of BTH (Derco et al., 2014; Fiehn et al., 1998; Liao et al., 2018; Zajíčková and Párkányi, 2009, 2008). BTH-Me is present in 16 % of the analyzed samples, whereas BTH and BTH-OH were detected in amounts above MQL only in 2 %. The low occurrence of BTH and BTH-OH differs from what has been observed in urban aerosols in the Po Valley (Favaro et al., 2024; Mazzi et al., 2025). Given that ozonation, direct photolysis and reactions with atmospheric radicals are reported to be effective in degrading BTH (Borowska et al., 2016; Karimova et al., 2024), a possible explanation is that BTH-OH resulting from the degradation of BTH undergoes further transformation during atmospheric transport, forming byproducts which were not targeted by this study (Liao et al., 2018). Considering that initial concentrations of BTH-SH in the alpine environment are lower than those typically observed in urban areas, the concentration of its degradation products is expected to be correspondingly lower and often below the MQL.

BTH-NH_2 is used as building block for the synthesis of more complex compounds that have applications in pharmaceuticals, biology and materials science (Dadmal et al., 2018; Javahershenas et al., 2024); it is also used as intermediate in the production of azo-dyes (Al-Joboury et al., 2021). Despite its high detection frequency, the concentration levels of this compound in the analyzed samples are low, with a median value of 0.2 ± 0.1 pg m^{-3}, representing only 1 % of ΣBTHs. Limited literature is available on the presence of this compound in the atmosphere of remote areas; however, the concentrations of BTH-NH_2 in urban aerosols are also low compared to other BTHs (Favaro et al., 2024; Mazzi et al., 2025; Nuñez et al., 2020). BTH-NH_2 is a relatively stable compound (Bunescu et al., 2008): studied its degradation via microbial and photochemical processes and observed no photodegradation after 125 h of irradiation by direct photolysis, and only low biotransformation. A recent study by Barbaro et al. (2024b) linked BTH-NH_2 presence in the Arctic atmosphere to a local natural source, possibly deriving from degradation processes catalyzed by marine or terrestrial biomass and snowmelt mobilization. In contrast to the Arctic observations, where BTH-NH_2 peaks in summer, at MRG the highest concentrations occur from springtime. The lack of clear correlation with MSA and arabitol (tracers of biogenic inputs) suggest that natural biogenic sources are not predominant at this site. Nonetheless, the highest springtime concentration could be partially influenced by snowmelt, which occurs earlier in alpine regions than in the Arctic, potentially releasing compounds

locally formed in the snowpack. It should be noted that the contribution of natural sources to BTH-NH_2 has not been fully elucidated yet, and further focused investigations are necessary to confirm their existence.

BTH-SCNMeS is a widely applied biocide in leather, paper, coatings and water-treatment industries and is highly toxic to aquatic organisms (Nawrocki et al., 2005). Sunlight-driven photolysis has however proven to efficiently transform BTH-SCNMeS into less harmful byproducts (Bertoldi et al., 2020; Brownlee et al., 1992) and this could explain its low concentrations in the analyzed samples, which are in agreement with those found in urban settings (Favaro et al., 2024; Mazzi et al., 2025). Identified transformation products include BTH-SH, BTH-OH and BTH (Bertoldi et al., 2020; Brownlee et al., 1992; Derco et al., 2014; Fiehn et al., 1998), which undergo further degradation as discussed above.

3.2. Occurrence of OPFRs in alpine aerosol

Of the six OPFRs analyzed, only three were detected in amounts above MQL in PM_{10}. TCEP was the most frequently detected compound (49 % of samples), followed by TCPP (43 %) and TPP (27 %) (Fig. 1). These detection frequencies are consistent with global trends in production and use of these FRs and with their chemical properties. Huang et al. (2022) conducted an extensive survey in an attempt to estimate the annual production volume of OPFRs and data collected evidenced that TCEP, TCPP and TPP are among the most widely produced and used compounds. Previous monitoring campaigns in both urban and remote environments similarly reported TCEP and TCPP as the dominant airborne OPFRs (Möller et al., 2012, 2011; Sühring et al., 2021; Zhang et al., 2022). The total concentration of OPFRs (ΣOPFRs) ranged from 0.3 ng m^{-3} to 10 ng m^{-3}. These concentration levels are more comparable to those found in urban settings in past years rather than remote ones, reflecting the increasing rate of OPFRs' emission in the environment in recent years due to the progressive replacement of BFRs.

TCEP – which exhibited the highest individual concentration, ranging from 0.2 to 10 ng m^{-3} – is extensively applied in domestic products (e.g. plastics, furniture, textiles, electronics, upholstery), building materials (e.g. paints, glues, coatings) and automotive parts (Bekele et al., 2021; Blum et al., 2019; Maddela et al., 2020; Wei et al., 2015). It is also the most common chlorinated OPE in polyurethane foams (PUFs) (Maddela et al., 2020). TCPP was the second most abundant compound (ranging from 0.1 to 6.8 ng m^{-3}) and is similarly used in household furnishing and upholstery, textiles, PUFs, car interiors and construction materials (Bacaloni et al., 2008; Bekele et al., 2021; Marklund et al., 2005a). TPP is predominantly used in polyvinyl chloride (PVC), thermoplastics, phenolic resins and electronics, as well as in lubricants and hydraulic fluids for its antiwear properties (Bekele et al., 2021).

Although TMP and TEP are also produced in high volumes (Huang et al., 2022), their low detection frequency in PM_{10} is likely due to their higher volatility and lower molecular weight, which favor partitioning into the gas phase. Gas-particle partitioning behavior is a critical factor influencing atmospheric persistence and transport of OPEs but remains underexplored (Li et al., 2025; Y. Wang et al., 2020) and it is not investigated in this paper. Furthermore, experimental evidence suggests that chlorinated OPFRs, having lower vapor pressure and a greater affinity with particulate matter, tend to dominate the particle phase of aerosols, while non-halogenated-alkyl OPFRs are more often associated with the gas phase (Li et al., 2025; Ma et al., 2022; Zhang et al., 2019). Aryl-OPFRs exhibit an intermediate behavior: while more prone to gas phase partitioning than chlorinated OPFRs, they still show a greater tendency to associate with particles than alkyl-OPFRs (Li et al., 2025; Zhang et al., 2022). This intermediate behavior explains the low concentrations of TPP – which was the least abundant compound in PM_{10}, with concentrations ranging from 5 pg m^{-3} to 0.2 ng m^{-3} – despite its widespread use. Moreover, studies have shown that the atmospheric transformation of OPFRs is structure-dependent: chlorinated OPFRs degrade more slowly than alkyl- or aryl-OPFRs under photochemical conditions, leading to increased persistence in the environment (Liu and Mabury, 2018; Liu et al., 2014; Mäkie et al., 2012; Tang et al., 2025). This may further contribute to the elevated particle-phase concentrations of TCEP and TCPP observed in this study.

The trend of TPP (Fig. S3) shows that it is almost absent in PM_{10} during spring and early summer, while its concentration increases in late summer and autumn. This can be partly explained by the temperature-dependent gas–particle partitioning of OPFRs: higher ambient temperatures favor partitioning into the gas phase, reducing particulate-phase concentrations, whereas cooler conditions in late summer and autumn promote reassociation with particles. Similar temporal shifts have been observed for other OPFRs in previous studies (Li et al., 2025; Yaman et al., 2020) and are consistent with the intermediate partitioning behavior of TPP compared to chlorinated and alkyl OPFRs.

To identify OPFRs' relative source contributions and variability in the high mountain area, particularly regarding consumer-product versus construction or industrial emissions, we propose here for the first time the use of the ratio between TCPP and TCEP. Rigid PUFs, primarily used in construction and industrial applications, typically contain higher concentrations of TCPP than flexible PUFs, commonly found in household and personal comfort products (Estill et al., 2020). Based on this distinction, the TCPP/TCEP ratio provides a qualitative indication of the relative contribution of these sources: a predominance of TCPP over TCEP suggests a relative prevalence of construction-related emissions, whereas a predominance of TCEP is more indicative of prevalence of consumer products emissions. In PM_{10} samples collected at MRG, TCPP/TCEP ratio had a median value of 0.8, with an interquartile range (IQR) of 1, suggesting a general predominance of consumer-related sources over the sampling period. This interpretation is consistent with the temporal trend of the individual compounds (Fig. S4), where TCEP typically displays higher concentrations than TCPP. However, pronounced ratio peaks (16–22) occurred from 23rd April to 5th May (Fig. S5). During this period, road works took place on nearby state highway SS346 (Fig. S6), likely increasing the release of construction-related materials. Notably, TCPP values are consistently higher than TCEP from the beginning of the sampling period until the end of May, leading to an elevated TCPP/TCEP ratio during this timeframe (Fig. S4), but apart from the aforementioned road works it was not possible to confirm with certainty the presence of additional construction or maintenance activities in the surrounding area. Nonetheless, the relatively greater contribution of TCEP compared to TCPP during this period may still indicate inputs from construction materials that were not present during the rest of the campaign. Given the lack of previous applications in the literature, this ratio should be considered exploratory and its robustness and applicability will need to be confirmed by future investigations in different environmental contexts.

3.3. Temporal trends and transport processes

Due to limited detection frequencies of individual compounds, temporal trends were evaluated using ΣBTHs and ΣOPFRs, representing the total particulate-phase load of each contaminant class. The temporal trends of ΣBTHs, ΣOPFRs and PM_{10} are shown in Fig. 2. The PM_{10} mass concentration ranged from 0.5 to 39 μg m^{-3}, with a median value of 3 μg m^{-3}. These values are consistent with previous years' measurements at MRG (Barbaro et al., 2024a). The highest mean concentration occurred during astronomical summer (8 ± 9 μg m^{-3}), followed by autumn (7 ± 4 μg m^{-3}) and spring (4 ± 3 μg m^{-3}). Summer concentrations exhibit high variability due to two spikes of 25 μg m^{-3} between 21 and 25 June, and 39 μg m^{-3} between 19 and 26 July. The analysis of BTs (Fig. S7) during 21–25 June indicate air masses originating from North Africa and transporting Saharan dust, whereas during 19–26 July the BTs indicate the arrival of air masses from North America across the Atlantic. Such long-range transport events, previously detected at MRG (Barbaro et al., 2024a), are known to increase PM_{10} concentrations

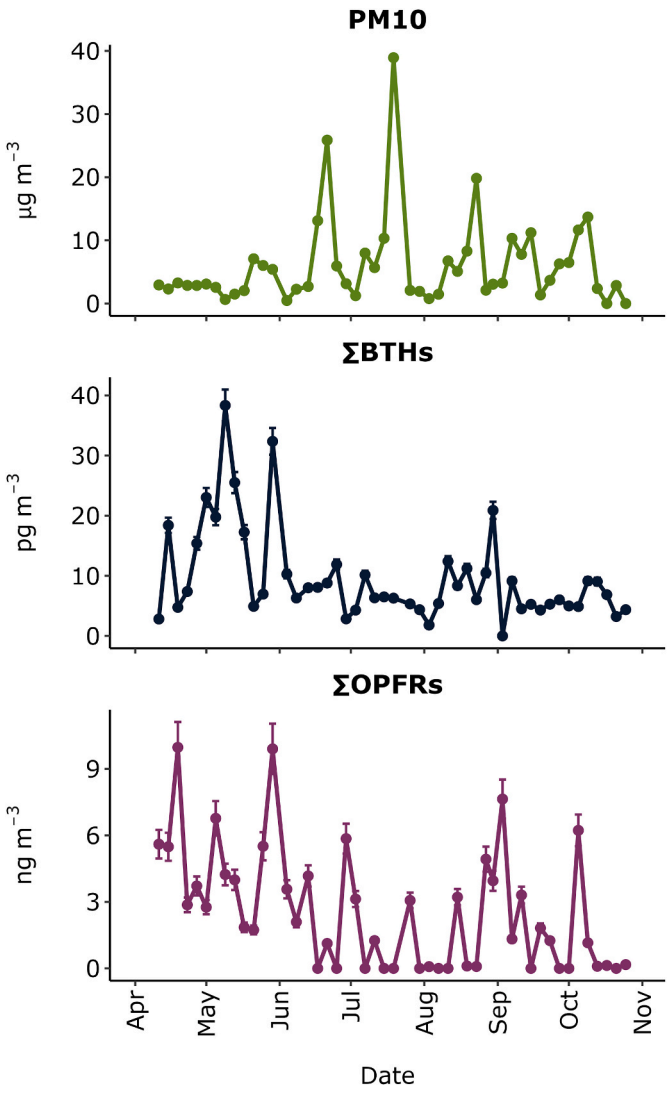

Fig. 2. Temporal trend of PM_{10}, ΣBTHs and ΣOPFRs concentrations at MRG from April to October 2023.

(Bukowiecki et al., 2016) and likely contributed to the observed peaks.

ΣBTHs and ΣOPFRs show a decreasing temporal pattern, with higher concentrations in spring. This trend can result from the combination of different atmospheric processes, such as thermal convection, mountain-valley breeze regimes and upward motion due to mixed-layer expansion, as highlighted in previous works (Feltracco et al., 2022; Vardè et al., 2022).

The effect of the valley breeze on the load of BTHs and OPFRs in the aerosol of MRG can be evaluated by calculating the daily average temperature lapse rate (TLR) during the sampling period. Valley breezes, which develop mainly on clear-sky days during the warm season, are characteristic features of the diurnal mountain wind system. They develop as a consequence of differential heating of adjacent air masses over complex topography, which result in pressure gradients that determine airflows that usually blow up-valley during daytime and down-valley during nighttime (Serafin and Zardi, 2010; Zardi and Whiteman, 2013). Winds blowing up the sides of a valley usually reach higher magnitudes than winds blowing downside and are generally stronger over valley sidewalls, compared to slopes on isolated mountainsides (Zardi and Whiteman, 2013). The greater the temperature difference from valley floor to mountain peak, the greater the intensity of the valley breezes. The occurrence of mountain and valley breezes is well documented in the Alps (Cantelli et al., 2017; Giovannini et al., 2017; Laiti et al., 2013), as well as their influence on pollution transport (De Franceschi and Zardi, 2009). This phenomenon has been previously observed at MRG (Barbaro et al., 2024a; Feltracco et al., 2022). In particular, Feltracco et al. (2022) demonstrated that wind typically arises in late morning and channels upward to the mountain peak, interacting with local up-valley flows, and that this circulation pattern tends to weaken during colder seasons (Barbaro et al., 2024a). evidenced a similar temporal trend concerning PM_{10}.

To calculate the average TLR, four weather stations located at different elevations (Table S3) were considered. As suggested by Feltracco et al. (2022), the weather stations were selected according to the main valleys that channel air masses toward MRG: in Veneto region, the Biois valley hosts the Agordo and Falcade stations; in Trentino Alto Adige, the San Pellegrino and Travignolo valleys host the Moena and Predazzo stations, respectively. No operating weather station was present at MRG during the sampling period, thus for estimating the TLR we used meteorological data from Passo Valles weather station, located about 10 km from MRG at 2042 m a.s.l., as representative for the high-altitude site. Fig. 3 represents the daily differential TLR (ΔTLR) with respect to April, which was chosen as baseline as it marks the beginning of the warm season, when valley breezes start to develop. For each hour of the day, the average TLR of April was subtracted from the corresponding average TLR of the other months, considering absolute values. The resulting ΔTLR curves indicate that May values are generally similar to April, with slightly higher values in the morning, suggesting marginally stronger valley breezes. In June, the average ΔTLR values gradually decrease; however, pronounced morning peaks still occur, reflecting the strong temperature gradient established by rapid valley heating under intense solar radiation. For the rest of the day, ΔTLR values remain relatively constant as the temperature gradient stabilizes. The negative ΔTLR values in September and October indicate smaller temperature differences between the valleys and the mountaintop, and therefore weaker valley breezes compared to the warm season. The minimal morning values and maxima around midday or early afternoon reflect the slower heating of the valley under weaker solar radiation, resulting in a delayed and less intense valley breeze. Overall, these patterns illustrate the temporal shift in the timing and intensity of valley breezes driven by solar heating.

In addition to valley breezes, seasonal changes in the planetary boundary layer (PBL) can also influence aerosol variability at MRG (Bukowiecki et al., 2016). The daily maximum PBL height is higher in summer (up to 1500 m a.g.l.) than in winter (500 m a.g.l.), due to

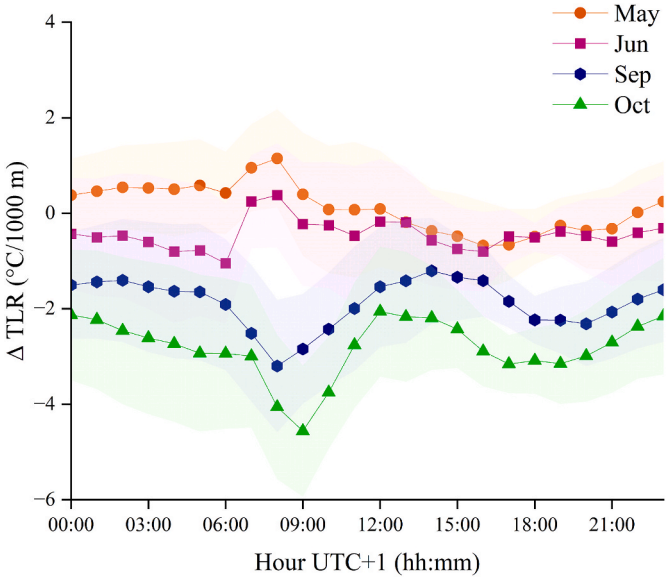

Fig. 3. ΔTLR with respect to April in May, June, September and October 2023.

stronger solar heating and more effective convective mixing (Vardè et al., 2022). This enhanced vertical mixing in spring and summer facilitates the upward transport of air masses from lower altitudes, which can reach MRG and influence the aerosol load and composition. In contrast, in colder seasons the shallower PBL limits vertical transport, reducing the impact of regional air masses on MRG aerosol.

3.4. Multivariate statistical analysis

To explore the correlation between the target emerging contaminants and other specific source tracers, HCA was applied to 15 variables and 49 samples. For the purpose of this statistical analysis, ΣBTHs and ΣOPFRs were treated as a single aggregated variable since most individual compounds had more than 50 % of missing values in the data matrix. As shown in the dendrogram in Fig. 4, three macroclusters were identified by considering a linkage distance above 10. The first cluster includes both ΣBTHs and ΣOPFRs, which are separated from other species by a linkage distance >15, and could be indicative of a purely anthropogenic signature since such chemicals are typically associated with human activity. Barbaro et al. (2024b) found a correlation between BTH-OH and BTH-NH_2 and biogenic inputs produced by algae and fungi in the Arctic environment, implying a natural local source for these compounds. However, as mentioned in Section 3.1, BTH-OH was present in only 2 % of our samples and BTH-NH_2 was found at low concentrations, therefore ΣBTHs in our dataset is more representative of anthropogenic sources rather than biogenic ones.

The second cluster groups major inorganic ions (Na^+, Mg^{2+}, Ca^{2+}, K^+, Br^-, NO_3^-, SO_4^{2-}) which mainly represent crustal inputs with a contribution from anthropogenic sources, as indicated by sulfate and nitrate (Barbaro et al., 2024a). The fact that these species cluster together, while ΣBTHs and ΣOPFRs remain isolated, indicates that the occurrence of the target contaminants is not associated with the main inorganic aerosol fraction. Instead, their separation highlights that emerging contaminants follow distinct dynamics, consistent with their attribution to specific anthropogenic activities.

The third cluster, dominated by organic constituents, is divided into two sub-clusters: one containing anhydrosugars (e.g. levoglucosan) which represent biomass burning (Barbaro et al., 2024a; Simoneit et al., 2004; Simoneit and Elias, 2001); the other including saccharides and alcohol-sugars, NH_4^+, MSA and CAs. Saccharides and alcohol-sugars are associated with biogenic emissions (Bauer et al., 2008; Feltracco et al., 2020). MSA is formed by the atmospheric oxidation of dimethyl sulfide (DMS), a compound released by phytoplankton (Gondwe et al., 2003), possibly originating from alpine lakes. CAs can be produced by photochemical oxidation of volatile organic compounds and their association with other biogenic tracers indicates that they likely represent biogenic

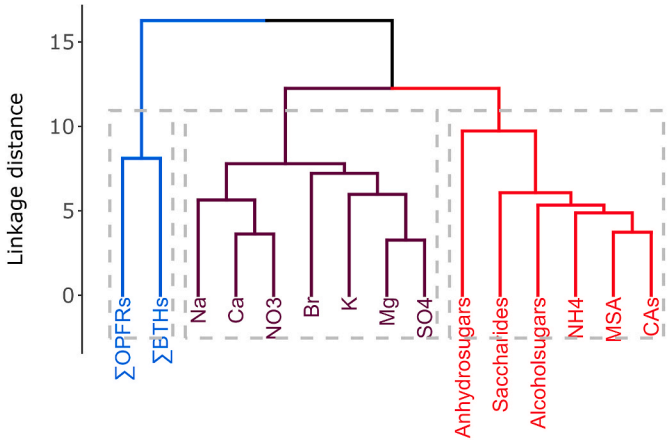

Fig. 4. Dendrogram resulting from HCA applied to 15 variables found in PM_{10} samples collected at MRG.

secondary organic aerosols originating from the oxidation of organic precursors released by local lakes (Barbaro et al., 2024a, 2020; Kawamura and Bikkina, 2016).

In support of the HCA, a PCA was applied to the same variables. PC1 and PC2, represented in Fig. S8, together explain 64 % of the total variance, with PC1 accounting for 51 % and PC2 for 13 %. PC1 is primarily driven by biogenic and crustal tracers, which have the highest positive loadings, while ΣBTHs and ΣOPFRs have negative loadings and are clearly separated from the other species, pointing to a distinct anthropogenic origin likely linked to site-specific human activities. PC2 further differentiates aerosol constituents, with inorganic species exhibiting negative loadings whereas positive loadings are associated with organic and biogenic markers. Overall, the PCA confirms the HCA results, revealing a clear separation of aerosol constituents based on their dominant sources and reflecting the complexity of regional-scale atmospheric processes contributing to aerosol composition at the high-altitude site.

4. Conclusions

This study presents the first assessment of background concentration levels of BTHs and OPFRs in atmospheric aerosol at a high-altitude site in the Eastern Italian Alps, revealing that both classes of compounds are detectable even in remote mountain environments. Their levels and temporal patterns are controlled by a combination of thermally driven wind regimes, upward transport associated with mixed-layer expansion and episodic long-range transport events.

The most abundant benzothiazole derivative was found to be BTH-SO_3H, one of the major byproducts of the degradation of BTH-SH, which is the most widely used as vulcanization accelerator in rubber and rubber products manufacturing. This result suggests that the resuspension of particles originally derived from tyre wear represents a major source of airborne BTHs. Considering the wide range of applications of this class of chemicals, other sources can't be excluded but their accurate identification is prevented by the absence of available data on their specific production and use.

This study highlights that TCEP and TCPP are the dominant OPFRs detected in PM_{10}, and that the predominance of TCPP during specific periods indicates episodic inputs from construction activities. The observed concentration levels align with the gradual replacement of BFRs by organophosphate alternatives. The differential detection frequencies and concentrations are influenced by chemical properties such as volatility and particle affinity, with chlorinated OPFRs showing greater atmospheric persistence due to slower degradation and stronger partitioning to particulate matter.

The multivariate statistical analysis supports a purely anthropogenic origin of both BTHs and OPFRs, possibly related to site-specific human activities.

Future year-round observations will be essential to fully capture seasonal variability and to further improve understanding of the environmental behavior of BTHs and OPFRs. In addition, future research should aim to identify the specific source regions and pathways of individual compounds, integrating receptor modelling and high-resolution atmospheric transport analyses.

CRediT authorship contribution statement

Eleonora Favaro: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Elena Barbaro:** Writing – review & editing, Methodology, Conceptualization. **Henri Diémoz:** Writing – review & editing. **Jacopo Gabrieli:** Writing – review & editing, Data curation. **Fabrizio De Blasi:** Writing – review & editing, Data curation. **Mara Bortolini:** Writing – review & editing, Data curation. **Andrei Munteanu:** Writing – review & editing, Formal analysis. **Giulio Cozzi:** Writing – review & editing, Data curation. **Warren R. L. Cairns:** Writing – review & editing, Funding acquisition. **Carlo**

Barbante: Writing – review & editing, Resources. **Andrea Gambaro:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Matteo Feltracco:** Writing – review & editing, Supervision, Methodology, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2025.127522.

Data availability

Data will be made available on request.

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