

Tyre-derived particles in size-segregated aerosols of urban and alpine areas: occurrence, sources and temporal trends



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OVERVIEW

Benzothiazoles (BTHs) are high production volume chemicals with various industrial applications and have emerged as significant contaminants due to their widespread usage and potential adverse effects on ecosystems and human health. 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. Being tyre-derived particles, they are often used as markers for traffic pollution based on their high detection frequencies in road runoff.

OBJECTIVES

- To determine eight BTHs in size-segregated urban aerosol and alpine aerosol.
- To characterize BTHs' particle size distribution in aerosol representative of the urban boundary layer.
- To assess regional differences and to observe seasonal trends.

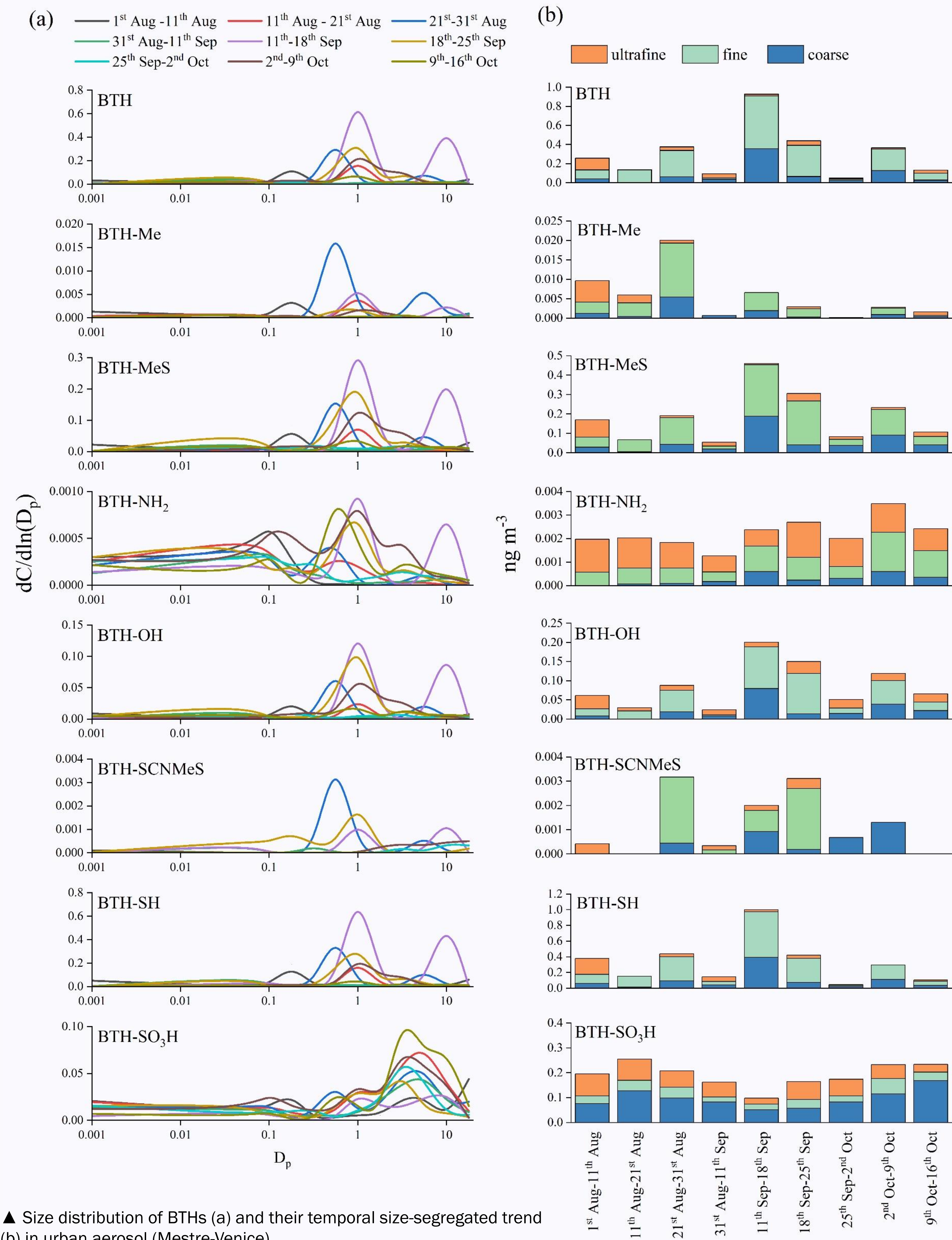
SAMPLING AND METHODOLOGY

MRG: PM₁₀ low volume sampler, Sep 2022 – Oct 2023, 96 h resolution.

Mestre-Venice: TSP twelve-stages cascade impactor, Aug – Oct 2023, 7 to 10 days resolution.

Analytical determination via **UHPLC-ESI-MS/MS** (Feltracco et al. 2023).

RESULTS



▲ Size distribution of BTHs (a) and their temporal size-segregated trend (b) in urban aerosol (Mestre-Venice).

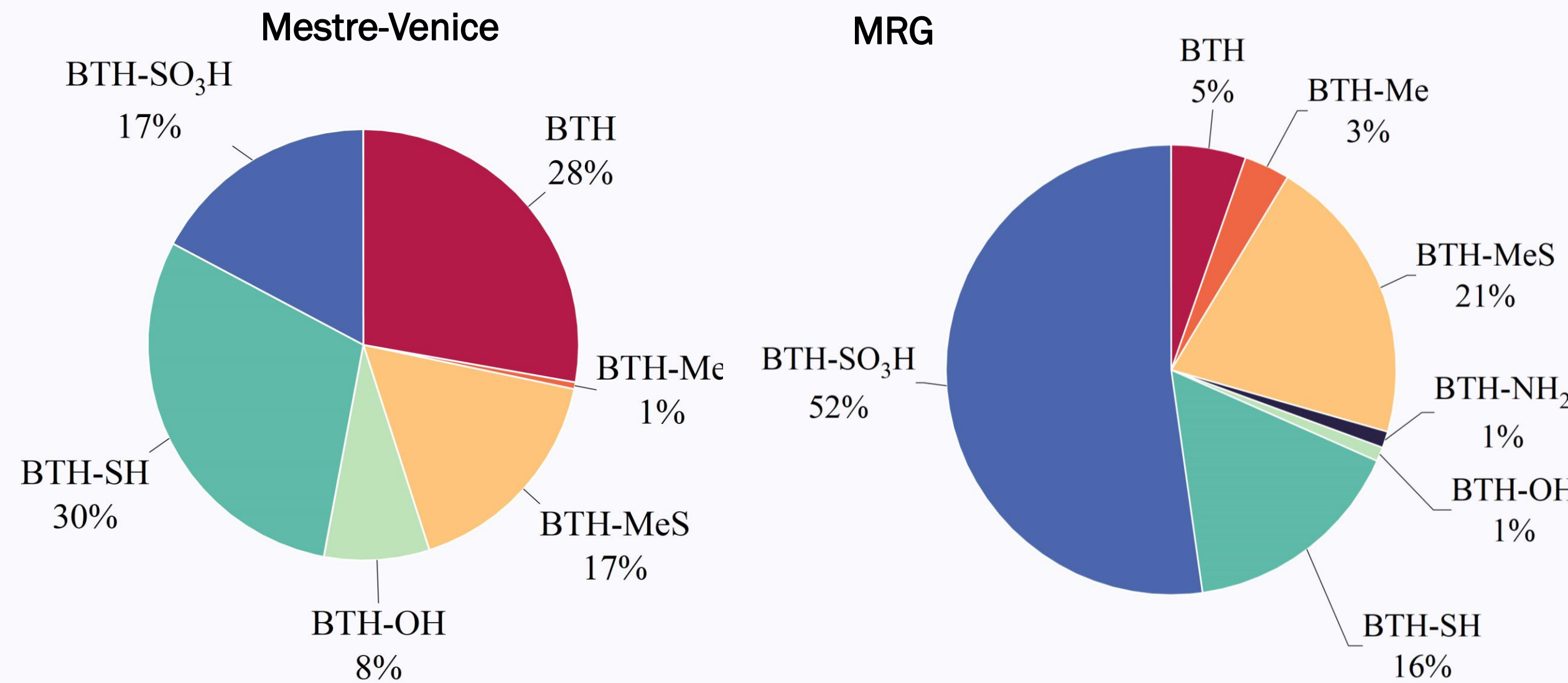
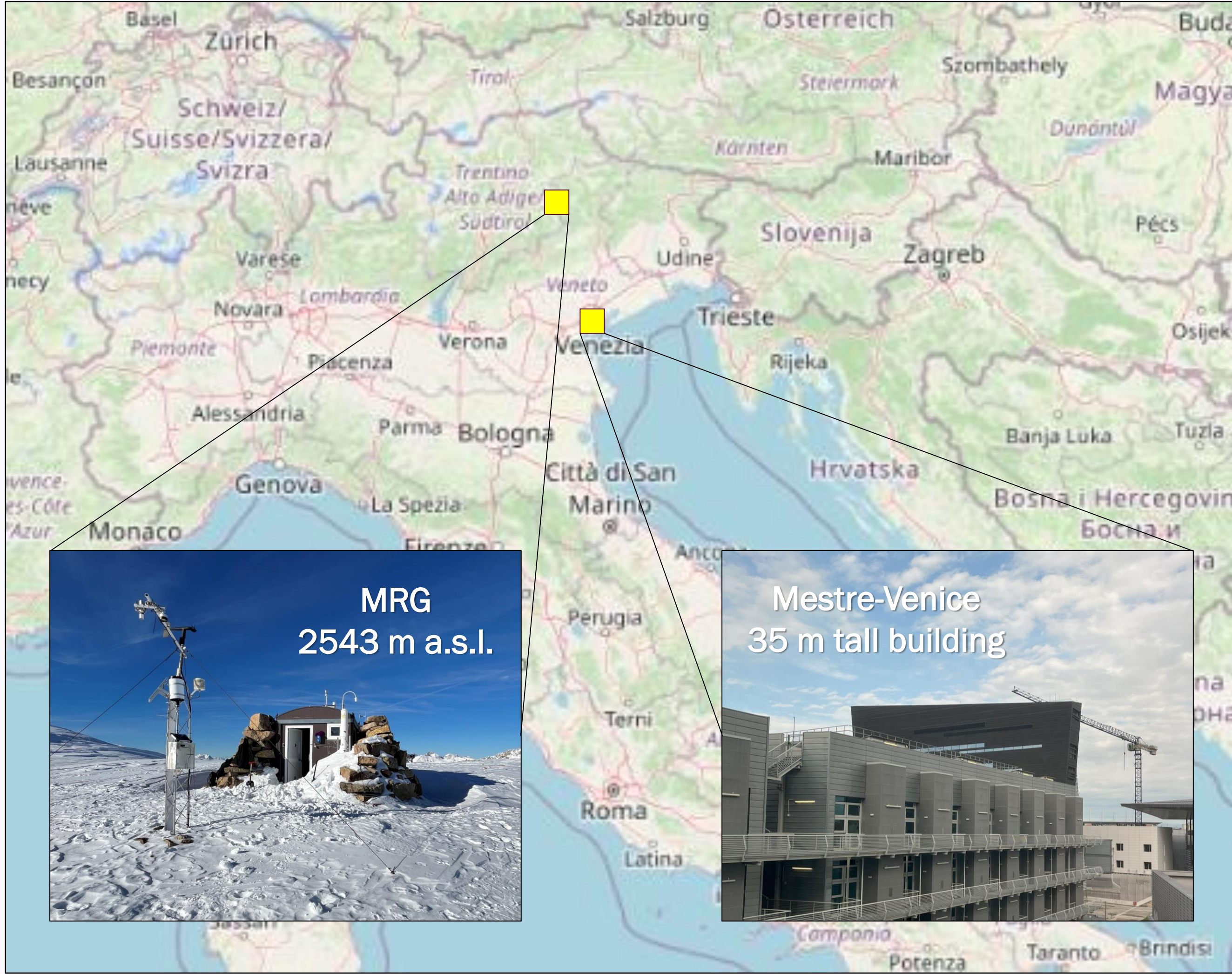
The dimensional distribution indicates an **enrichment of all BTHs in the fine fraction of urban aerosol**, probably due to two reasons:

- the peculiar orographic characteristics of the Po Valley, where our sampling site is located, which prevents atmospheric dispersion and air masses exchange and leading to an increase in the fine size fraction of aerosols (Maranzano 2022; Speranza and Caggiano 2023);
- 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 Brines et al. 2016; Chan and Kwok 2000; Schäfer et al. 2006).

FUTURE DEVELOPMENTS

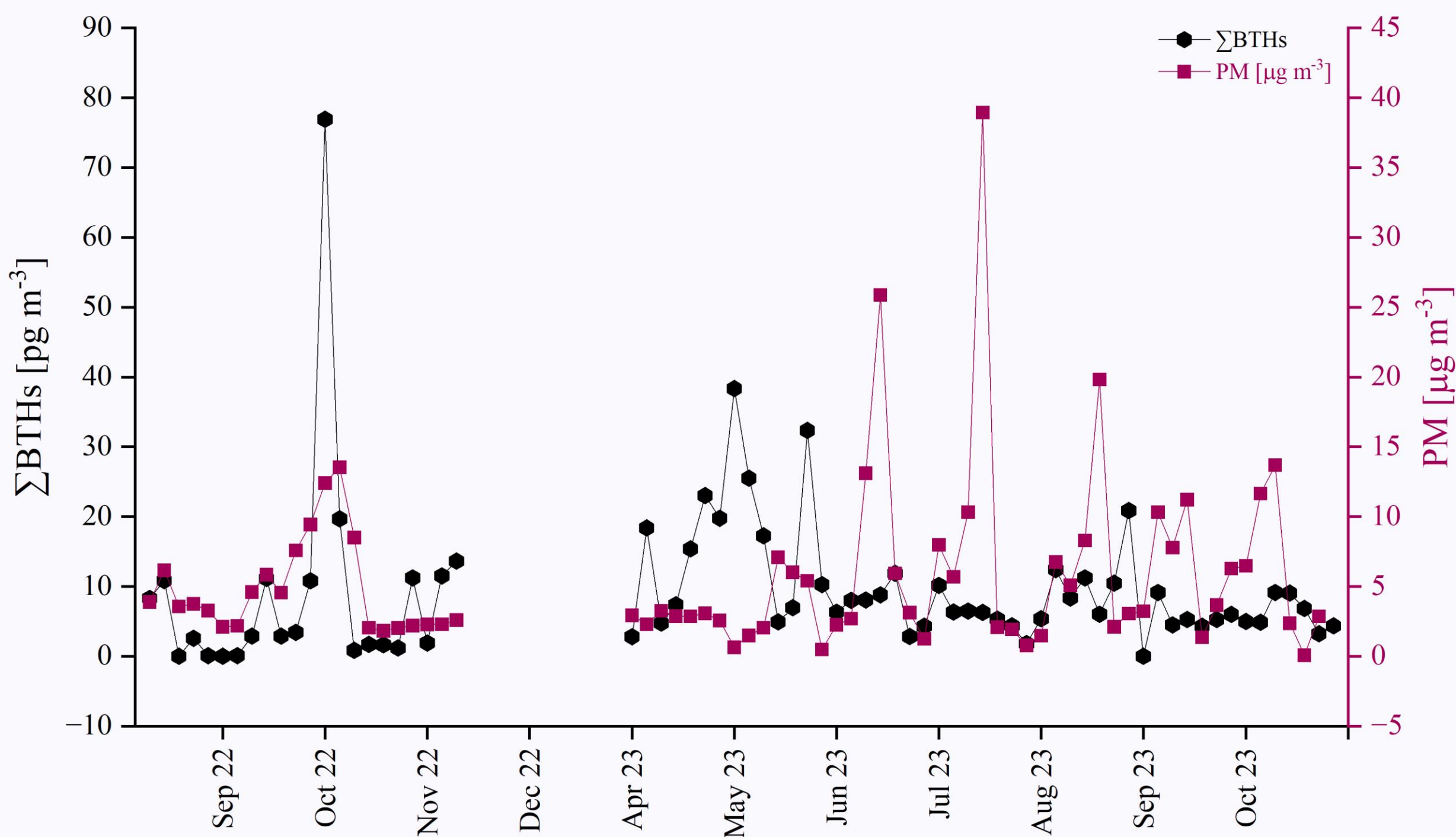
- For the urban area, more samples should be considered to monitor BTHs' seasonal trend and their vertical distribution in airborne particulate matter, since there could be differences in their dimensional distribution between street and rooftop level.
- For the alpine area, obtaining data on the size distribution of BTHs' in aerosol could offer insights on transport mechanisms. Moreover, a nighttime/daytime study could help assessing how variables such as solar radiation and typical alpine phenomena such as mountains and valley breezes can alter the contribution of the target compounds.

STUDY SITE



▲ BTH-SH, the main vulcanizing agent used in rubber manufacturing, has the highest relative mean abundance in urban aerosol, suggesting tyre debris as its main source. The highest relative mean abundance of BTH-SO₃H, its photodegradation product, in alpine aerosol suggest **photodegradation during atmospheric transport from valley to mountain**.

▲ BTH and BTH-OH have more significative abundances in the urban area than the alpine site. This could be due to their progressive removal during atmospheric transport.



▲ The sum of BTHs and PM₁₀ show a similar trend at MRG, except for the period Apr-May 2023. Higher concentration of PM₁₀ during summer can be due to:

- 1) **valley breezes**, which tend to be more intense in the warm seanson (Giovannini et al. 2015; Laiti et al. 2013);
- 2) a higher depth of the **planetary boundary layer** (Gabrieli et al. 2011, Vardè et al. 2022). As a result, air masses tend to channel upward carrying **contaminants from the valley**.

▼ High values of ΣBTHs in Apr-May are mainly due to the contribution of **BTH-SH**, possibly deriving from the **incursion of continental air masses** which occurred in this specific period as highlighted through Hysplit clustering algorithm.

