Occurrence and risk assessment of benzothiazole, benzotriazole and benzenesulfonamide derivatives in airborne particulate matter from an industrial area in Spain

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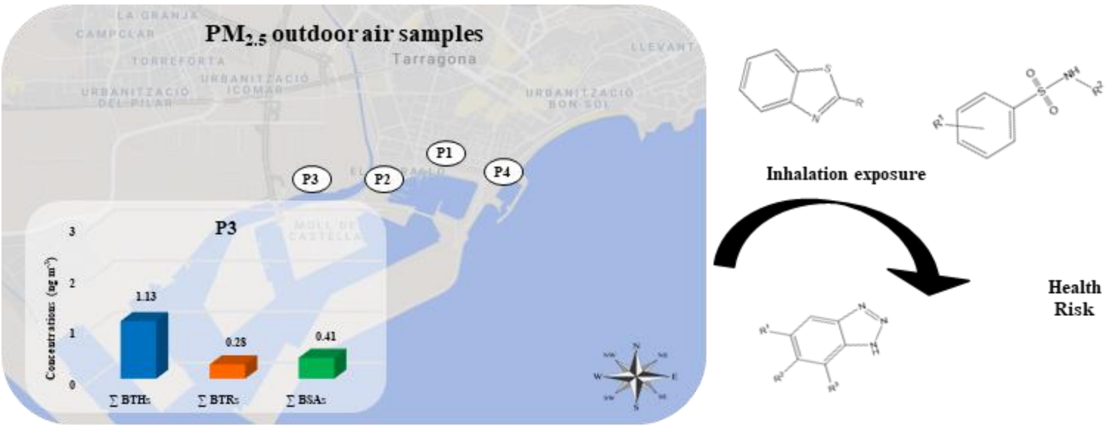
Graphical Abstract



Keywords: benzothiazoles, benzotriazoles, benzenesulfonamides, gas chromatography-mass spectrometry, particulate matter, port

Abstract

In this study we monitored benzothiazole (BTHs), benzotriazole (BTRs) and benzenesulfonamide (BSAs) derivatives in airborne particulate matter from four sampling sites near the port of Tarragona (Spain) over a one-year period. To do so, we developed a method based on ultrasound-assisted solvent extraction (USAE) followed by gas chromatography-mass spectrometry (GC-MS). We also studied concentrations of NO_2 and airborne particulate matter ($PM_{2.5}$ and PM_{coarse}) for a year. Our results showed NO_2 and $PM_{2.5}$ concentrations below the maximum average values established by the Europen Directive 2008/50/EC in the zone under study. Moreover, NO_2 values are directly proportional to changes in weather conditions and traffic emissions, while PM_{coarse} and $PM_{2.5}$ concentrations do not follow a clear trend as these may be generated from multiple sources (loading and unloading activities and traffic emissions). Regarding BTHs, BTRs and BSAs concentrations in particulate matter, the compounds found at the highest concentrations were 1-H-benzothiazole, 2-methylbenzothiazole, 2-chlorobenzothiazole, 1-H-benzotriazole, 4-methyl-1-H-benzotriazole, 2-(methylthio)-benzothiazole, 5-methyl-1-H-benzotriazole and bromobenzenesulfonamide with average concentrations ranging from 0.19 to 1.54 ng m^{-3} in PM_{coarse} and from 0.09 to 0.61 ng m^{-3} in $PM_{2.5}$. The remaining compounds were below the method quantification limits (MQLs) or were undetected in the samples analysed. Health risk values associated with the inhalation of the studied compounds were between 1.80×10^{-3} - 1.27×10^{-2} in the worst-exposure scenario.

1. Introduction

Air quality in port facilities has aroused the interest of the scientific community around the world over the last decade because of its potential impact on nearby urban environments (Murena et al. 2018; Xu et al. 2018). Initially, studies have mainly focused on monitoring major air pollutants emissions such as $PM_{2.5}$ and PM_{10} particles (Mamoudou et al. 2018; Xiao et al. 2018) and NO_2 and O_3 concentrations (Ledoux et al., 2018; Sorte et al., 2019), and determining the group of volatile organic compounds known as ozone precursors (Ohura et al. 2006; Xiao et al. 2018). However, recent years have seen a progressive increase in scientific articles focusing on the occurrence of high-volume emerging organic compounds such as phthalates and organophosphates (Aragón et al, 2012; 2013), flame retardants (Sutton et al., 2019) or plastic additives (Maceira et al., 2019) in both air and particulate matter from different industrial environments.

In this context, the presence of the group of emerging organic compounds consisting of benzothiazoles (BTHs), benzotriazoles (BTRs) and benzenesulfonamides (BSAs) has also been studied in various environmental samples. In fact, as these compounds are widely used, for example, as ultraviolet light stabilizers in textiles and plastics, in antifreeze formulations for automobiles and as intermediate products in the synthesis of drugs (Herrero et al., 2014a; Wan et al., 2016; Liao et al., 2018), they have been found at ppb or ppt levels in the following environmental media: influent and effluent waters (Asimakopoulos et al., 2013a; Salas et al., 2016), surface waters (Casado et al., 2014; Hidalgo et al., 2019), sewage sludge and sediments (Herrero et al., 2014b; Karthikraj et al., 2017), indoor dust (Wang et al., 2013; Ajibola et al., 2015), road tunnel particulate matter (Grung et al., 2017), and indoor and outdoor air samples (Xue et al.,2017; Maceira et al., 2018; Asheim et al., 2019). They have also been found in other kind of samples such as textiles and infant clothing (Liu et al., 2017) or playground pavers (Llompart et al., 2013) from which they can be released into the atmosphere through evaporation processes. Adverse health effects such as liver and kidney ailments, dermatitis and respiratory irritation after exposure to the above compounds have also been reported by some authors (Asimakopoulos et al., 2013b; 2013c; Avagyan et al., 2015; Wan et al., 2016). The most common human exposure pathway for these compounds is the ingestion of foods and beverages (Ginsberg et al., 2011). However, they can also be inhaled as their presence in the gaseous state and particulate matter in the atmosphere is favoured by volatilization and the erosion of materials that contain these compounds (Grinsberg et al., 2011; Maceira et al., 2018).

Because of the physicochemical properties of BTHs, BTRs and BSAs (their polar nature, high water solubility and relatively low volatility), liquid chromatography (LC) coupled with mass spectrometry (MS) or tandem mass spectrometry (MS/MS) as the detection technique is the most common separation technique for determining these compounds (Asimakopoulos et al., 2013b; Herrero et al., 2014a; Hidalgo et al., 2019). However, because of problems relating to isomer separation and high signal enhancement/suppression reported by Herrero et al. (2014a) and Asimakopoulos et al. (2013b) when analysing environmental samples using LC-MS/MS, gas chromatography-mass spectrometry (GC-MS) and GC-MS/MS have been found to be powerful alternatives. Accordingly, Xu et al. (2015) and Maceira et al. (2018) developed two GC-MS-based methods to determine this group of compounds in environmental samples with a good separation of isomeric compounds, a lower matrix effect and better selectivity than LC-MS-based methods. To obtain selective and sensitive methods for determining BTRs, BTHs and BSAs when analysing solid samples, various extraction techniques such as shaking (Zhang et al., 2011), Soxhlet (Zhang et al., 2011), ultrasound-assisted solvent extraction (USAE) (Avagyan et al., 2015), microwave-assisted extraction (MAE) (Speltini et al., 2016), pressurized liquid extraction (PLE) (Herrero et al, 2014c) and quick, easy, cheap, effective, rugged and safe (QuEChERS) (Herrero et al., 2014b) have been applied.

Due to the lack of information on the presence of benzothiazoles, benzotriazoles and benzenesulfonamides in outdoor air samples, we have monitored these compounds in airborne particulate matter samples ($PM_{2.5}$ and PM_{coarse}) from four sampling sites close to the port of Tarragona over a one-year period. A quick and simple method based on USAE followed by

GC-MS was also developed to simultaneously determine these compounds in particulate matter. In view of the concentrations found, human exposure through outdoor air inhalation (PM_{coarse} and $PM_{2.5}$) was calculated for three age groups and two exposure scenarios. Health risk assessment was also carried out for 1-H-benzothiazole and 1-H-benzotriazolesince, because they are the only studied compounds for which toxicological data are available.

2. Materials and methods

2.1. Chemical standards and reagents

The target compounds evaluated in this study can be divided into three families: benzothiazoles (BTHs), benzotriazoles (BTRs) and benzenesulfonamides (BSAs). More specifically, there were six BTHs: 1-H-benzothiazole (BT), 2-methylbenzothiazole (MeBT), 2-chlorobenzothiazole (ClBT), 2-(methylthio)-benzothiazole (MeSBT), 2-aminobenzothiazole (NH_2BT) and 2-hydroxybenzothiazole (OHBT); four BTRs: 1-H-benzotriazole (BTR), 4-methyl-1-H-benzotriazole (4TTR), 5-methyl-1-H-benzotriazole (5TTR) and 5,6-dimethyl-1-H-benzotriazole (XTR); and six BSAs: benzenesulfonamide (BSA), *ortho*-toluenesulfonamide (*o*-TSA), *para*-toluenesulfonamide (*p*-TSA), N-ethyl-*para*- toluenesulfonamide (Et-*p*-TSA), N-methyl-*para*-toluenesulfonamide (Me-*p*-TSA), and 4- bromobenzenesulfonamide (BrBSA). All commercial standards were provided by Sigma-Aldrich (Steinheim, Germany). The internal standards d4-benzothiazole (d4-BT), d4-benzotriazole (d4-BTR) and d4-*para*-toluenesulfonamide (d4-*p*-TSA) were also supplied by Sigma-Aldrich. Individual standard solutions of the target compounds were prepared in ethyl acetate at a concentration of 1,000 ng μL^{-1} and stored in the fridge at 4 ºC. A working solution containing all the target compounds at 100 ng μL^{-1} in ethyl acetate was made on the day of use and stored in the dark at 20 ºC.

The ethyl acetate with a purity over 99.9% (GC grade) was used for the standard solutions and to perform the extractions (J.T. Baker, Deventer, Netherlands). Helium gas with a purity of 99.999% was used for the chromatographic separation (Carburos Metálicos, Tarragona, Spain).

2.2. Sample collection

PM_{coarse} (2.5 - 10 µm) and $PM_{2.5}$ (≤ 2.5 µm) airborne particulate matter samples of outdoor air were collected from four sampling sites close to the port of Tarragona over a one-year period (November 2017 -2018). Fig. 1 shows the distribution and exact location of each sampling site in the port of Tarragona. With a total movement of roughly 35 million tons per year (MT $year^{-1}$), the largest volume of traffic in the port of Tarragona corresponds to energy products such as coal and petroleum coke (24 MT $year^{-1}$), followed by agri-food products (5 MT $year^{-1}$) and chemical products (2 MT $year^{-1}$). The port of Tarragona also has a small refinery and a storage facility to facilitate the import and export of chemical products (AP, 2018). As reported by some authors in the field (Xiao et al., 2018; Xu et al., 2018; Sorte et al., 2019), the daily loading and unloading of goods plus road and rail transportation and shipping are expected to affect air quality due to the continuous emission of particulate material of various sizes.

A total of 96 samples were taken (48 of each particulate size) at the rate of one sample per month at each sampling site. PM_{coarse} and $PM_{2.5}$ samples were simultaneously collected on 47 mm Ø micro-fibre quartz filters with a TEOM® 1405-D Dichotomous Ambient Particulate Monitor, both of which were provided by Thermo Fisher Scientific (Barcelona, Spain). After 30 days of sampling under a constant flow-rate of 0.0017 m^3 min^{-1}, the total volume for PM_{coarse} samples was 72.14 m^3. After 30 days of sampling under a constant flow-rate of 0.0030 m^3 min^{-1}, the total sampling volume for $PM_{2.5}$ samples was to 129.60 m^3. Aluminium foil was used to wrap the samples before they were placed inside sealable plastic bags and stored in the freezer until analysis. Meanwhile NO_2 concentrations were online recorded at sampling site P2 (see Fig. 1.) using the nitrogen oxides chemiluminescence analyser 9841 from MCV (Collbató, Barcelona, Spain).

2.3. Analytical Method

Air samples were analysed for the target compounds using the following procedure. PM_{coarse} and $PM_{2.5}$ filters were extracted with 5 mL of ethyl acetate in 20 mL glass vials using ultrasound for 15 min. The extracts were then filtered using 0.22 µm PTFE syringe filters.

After adding 400 µL of dimethylformamide (98% purity, Sigma-Aldrich), the extracts were evaporated under a gentle stream of nitrogen to dryness. The extracts were reconstituted with 100 µL of ethyl acetate containing the ISs at a concentration of 2.5 ng µL^{-1} and analysed by GC-MS. The mean recovery rates (*n* = 3, 0.5 ng) ranged from 82% to 97% regardless of target compound or type of filter analysed, with relative standard deviations below 6% in all cases (see Table 1S).

Chromatographic analysis was performed by gas chromatographic separation on a GCMS-QP2010 Ultra High-Performance Gas Chromatograph Mass Spectrometer from Shimadzu Corporation (Izasa S.A., Madrid, Spain) with electron impact ionization and a single quadrupole as analyser. The GC-MS was also equipped with a split/splitless injection port and an autosampler from Shimadzu. For the chromatographic analysis, 2 µL injections were performed in splitless mode at 300 ºC. The GC separation was carried out with a 30 m × 0.25 mm ID capillary column, with a film of 0.25 µm of 50% phenyl-50% dimethylpolysiloxane obtained as Zebron ZB-50 (Phenomenex, Torrance, CA, USA). Helium was used as carrier gas at a constant flow of 1.2 mL min^{-1}. The oven temperature programme was as follows: the initial temperature of 80 ˚C was increased by 10 ˚C min^{-1} to 180 ºC and then by 20 ºC min^{-1} to 320 ºC (3 min). Transfer line and ion source temperatures were fixed at 280 ºC and 230 ºC, respectively. A filament-multiplier delay of 4 min was set to prevent instrument damage. To improve the selectivity and sensitivity of the analytical method, quantitative analysis was performed in selected ion monitoring (SIM) mode. Table 1S shows the retention times and quantifier and qualifier ions of the target compounds as well as the ISs.

Calibrations were performed as a multistep internal standard calibration to ensure accurate values and reliable calibration curves (Maceira et al., 2018). All target compounds showed good linearity up to 10 ng µL^{-1}, with determination coefficients (r^2) above 0.998 in all cases. The lowest calibration point, which was defined as the instrumental limit of quantification (LOQ), showed a signal-to-noise ratio of over 10 and well-defined peaks (Gaussian shape) for each target compound. Instrumental limits of detection (LODs, signal-to-noise ratio of three) and intra-day and inter-day repeatabilities were also calculated (n = 5, 0.5 ng µL^{-1}). These results are shown in Table 1S.

3. Results and discussion

In this section we present the results of outdoor air sampling conducted between November 2017 and November 2018 at four monitoring sites near the port of Tarragona. More specifically, the presence of the emerging organic compounds BTHs, BTRs and BSAs in PM$_{coarse}$ and PM$_{2.5}$ samples was closely monitored for a year due to the widespread use of these compounds in industry and household products (Herrero et al. 2014; Wan et al. 2016; Maceira et al. 2018). NO$_2$, PM$_{coarse}$ and PM$_{2.5}$ concentrations were also recorded in order to determine how the daily activities conducted in the zone under study influence the generation of these compounds.

3.1. Quality assurance parameters

To ensure the reproducibility and quality of the results, some preventive measures have been taken. Accordingly, n=5 blanks of the 47 mm Ø micro-fibre quartz filters used to collected PM$_{coarse}$ and PM$_{2.5}$ samples were done. Only BT was detected in the blanks performed and always at concentrations below LOQ. Afterwards, the extraction method described in section 2.3. was applied to check the recoveries in real airborne PM$_{coarse}$ and PM$_{2.5}$ samples. To do so, the 47 mm Ø micro-fibre quartz filters were cut into two parts. One part provided us target compounds concentrations in the airborne PM$_{coarse}$ and PM$_{2.5}$ samples and the other was spiked at 0.5 ng µL^{-1}. No significant differences were observed between the recoveries in PM$_{coarse}$ and PM$_{2.5}$ samples with values between 82% (ClBT, PM$_{coarse}$) and 97% (*o*-TSA, PM$_{2.5)}$ and RSD values between 2.8% (MeBT, PM$_{2.5}$) and 5.7% (BrBSA, PM$_{coarse}$). Quantification of the target compounds in the airborne particulate matter samples analysed was performed by internal standard calibration and recoveries were taken into account to obtain the final sample concentration.Before analysing the samples, and to ensure that the analytical method enabled the detection and/or quantification of the target compounds at trace levels in airborne particulate matter of outdoor air samples, method detection limits (MDL) and quantification limits (MQL) were determined for each sampling volume taking into account the recoveries of each compound. As Table 1 shows, PM_{coarse} MDLs (volume = 72.14 m^{-3}) ranged from 0.002 ng m^{-3} to 0.06 ng m^{-3} except for 5TTR with 0.14 ng m^{-3}. $PM_{2.5}$ MDLs (volume = 129.60 m^{-3}) ranged from 0.001 ng m^{-3} to 0.04 ng m^{-3} and up to 0.08 ng m^{-3} for 5TTR (see Table 2). MQLs ranged from 0.003 ng m^{-3} to 0.14 ng m^{-3} for PM_{coarse} and from 0.002 ng m^{-3} to 0.08 ng m^{-3} for $PM_{2.5}$. Higher MQLs were found for 5TTR with values of 0.35 ng m^{-3} and 0.20 ng m^{-3} for PM_{coarse} and $PM_{2.5}$, respectively.

3.2. PM_{coarse} and $PM_{2.5}$ samples

The evolution throughout the year of the daily average values of PM_{coarse} and $PM_{2.5}$ online recorded at the four sampling sites under study as well as the NO_2 concentrations found at P2 are shown in the column graphs in Fig. 1S.

PM_{coarse} values ranged from 4.12 µg m^{-3} at site P3 to 19.1 µg m^{-3} at site P2. $PM_{2.5}$ concentrations, on the other hand, ranged from 3.84 µg m^{-3} to 23.3 µg m^{-3}. Both of these values were recorded at site P4. Overall, PM_{coarse} concentrations were found to be higher than $PM_{2.5}$ concentrations at all the sampling sites evaluated except for site P3 between June and September 2018 and site P4 in October 2018. The concentrations of $PM_{2.5}$ were always below the maximum of 25 µg m^{-3} set as annual average by European Directive 2008/50/EC (ED, 2008) and Spanish royal decree 102/2011 (RD102, 2011). NO_2 concentrations in P2 ranged from 11.9 to 31.5 µg m^{-3}, which in no case exceed the 40 µg m^{-3} set as annual average by the regulations mentioned above (EU2008/50, 2008; RD102, 2011).

Unlike what was observed with regard to NO_2 values from site P2, the PM_{coarse} and $PM_{2.5}$ values found in the port area did not follow a clear trend associated with changes in weather conditions, such as the thermal inversion episodes characteristic of winter in the area under study or the increase in temperatures characteristic of the spring and summer (METEO, 2018). A possible explanation for this is that NO_2 is mainly generated by traffic-related combustion processes (Sharma et al. 2016; EEA, 2018b), while PM_{coarse} and $PM_{2.5}$ particles (EEA, 2018a) may be generated from multiple sources, including the loading and unloading activities that take place every day in the zone under study. More specifically, the handling of coal and agri-food products such as cereals, feed and fertilizers at the port may contribute significantly to the generation of particulate matter of multiple particle sizes. This is also corroborated by results published by Xu et al. (2018), who analysed $PM_{2.5}$ samples from a port located on the south-eastern coast of China.

3.3. *BTHs, BTRs and BSAs*

A total of 12 PM_{coarse} and 12 $PM_{2.5}$ samples were taken to monitor the concentrations of BTHs, BTRs and BSAs at each of the sampling sites close to the port of Tarragona between November 2017 and November 2018. Tables 1 and 2 show our results, including the ranges of concentration and the arithmetic means expressed in ng m^{-3} and particles concentrations expressed in µg m^{-3}.

The results from our analysis of PM_{coarse} and $PM_{2.5}$ particulate matter samples showed that the most representative target compounds were: BT, MeBT, ClBT, BTR, 4TTR, MeSBT, 5TTR and BrBSA. Fig. 2 shows the mean, the maximum, the minimum, and the 25th, 50th (median) and 75th percentile of these compounds. The remaining compounds were mainly undetected or were detected at concentrations below the MQLs, while XTR was not detected in any of the 96 samples analysed. Me-*p*-TSA was only detected in some samples taken at sampling site P1 and always at concentrations below the MQLs. As you can see in Tables 1 and 2, Et-*p*-TSA and *o*-TSA were detected only at sites P2 and P3 and at concentrations below the MQLs, while *p*-TSA was detected in all sampling sites under study but not at quantifiable levels.

The most representative compounds generally followed a positively skewed asymmetric distribution of the results, with a concentration mean higher than the median, while 5TTR followed a symmetric distribution of the results (median = mean). With regard to PM_{coarse}

samples, MeBT and MeSBT had the widest ranges of concentration (from n.d. to 9.79 ng m^{-3} for MeBT and from n.d. to 17.1 ng m^{-3} for MeSBT). In contrast, 5TTR had the narrowest range of concentration, with values ranging from n.d. to 0.92 ng m^{-3} in PM_{coarse} samples. The same trend, but with slightly lower concentrations, was observed for $PM_{2.5}$ samples, with concentrations ranging from <LQM to 1.85 ng m^{-3} for MeBT, from n.d. to 10.8 ng m^{-3} for MeSBT and from n.d. to 0.48 ng m^{-3} for 5TTR.

With respect to the average concentrations for the most characteristic target compounds in PM_{coarse} samples, the highest value was 1.54 ng m^{-3} for MeSBT while the lowest values were 0.20 ng m^{-3} and 0.19 ng m^{-3} for 4TTR and 5TTR, respectively. The other compounds in Fig. 2 showed average concentrations between 0.26 ng m^{-3} for BTR and 1.24 ng m^{-3} for MeBT. The maximum and minimum average concentrations for $PM_{2.5}$ samples were 0.61 ng m^{-3} and 0.09 ng m^{-3} for MeSBT and 4TTR, respectively. The average values for the remaining compounds in Fig.2 ranged from 0.56 ng m^{-3} for BT and 0.13 ng m^{-3} for 5TTR.

Overall, the target compounds found at the highest concentrations in both the PM_{coarse} and $PM_{2.5}$ particulate matter samples analysed were BTHs. All BTRs included in this study, except XTR, were also detected in PM_{coarse} and $PM_{2.5}$ samples but at lower concentrations or below the MQLs. Regardless of the kind of sample analysed, the only BSA found at concentrations higher than MQLs was BrBSA. ∑BTHs values between 2.27 ng m^{-3} and 4.71 ng m^{-3} for PM_{coarse} and between 1.13 ng m^{-3} and 2.60 ng m^{-3} for $PM_{2.5}$ were obtained. ∑BTRs concentrations dropped to between 0.49 ng m^{-3} and 0.78 ng m^{-3} for PM_{coarse} and between 0.26 ng m^{-3} and 0.49 ng m^{-3} for $PM_{2.5.}$ Even lower were the ∑BSAs values for PM_{coarse} (between 0.28 ng m^{-3} and 0.49 ng m^{-3}) and for $PM_{2.5}$ (between 0.15 ng m^{-3} and 0.41 ng m^{-3}) samples. Also, as Fig. 2S shows, the lowest and highest total concentrations (∑ (BTHs + BTRs + BSAs)) were found at sampling sites P3 and P4 for both PM_{coarse} (3.05 ng m^{-3} and 5.84 ng m^{-3}) and $PM_{2.5}$ (1.83 ng m^{-3} and 3.19 ng m^{-3}) particulate matter samples. Moreover, the concentrations of the target compounds found in PM_{coarse} samples were higher than those in $PM_{2.5}$ samples, which means that these compounds tended to accumulate in particulate matter whose sizes ranged from 2.5 µm to 10 µm (e.g. dust, pollen, fly ash, etc.) rather than in fine particles ($PM_{2.5}$). The concentrations of target compounds found in particulate matter were directly proportional to the concentrations of particles, especially for PM_{coarse} samples. As with particles, target compounds concentrations not showed seasonality effect probably due to the widespread use of the target compounds especially in an area of high commercial activity as the zone under study.

The obtained results agree with the findings reported by Asheim et al. 2019, who analysed airborne particulate matter (PM_{coarse} and $PM_{2.5}$) from an urban road of Trondheim (Norway). In both cases BTHs were the compounds found at the highest concentrations in PM_{coarse} and $PM_{2.5}$ samples, while BTRs were present at lower concentrations. In contrast, Maceira et *a*l. (2018) found BTRs at concentrations higher than BTHs in PM_{10} punctual samples from Tarragona with BTR, 4TTR and 5TTR as the most characteristic compounds. BSAs were the compounds found at the lowest concentrations in the present study (PM_{coarse} and $PM_{2.5}$) and in the PM_{10} samples analysed by Maceira et al., (2018). BTHs, BTRs and BSAs concentrations reported in outdoor air particulate matter were always lower than those reported by Xue et al. (2017) and Wan et al. (2016) in indoor air particulate matter samples from car parks, cars, public places, offices, laboratories and homes in Albany (New York, USA).

3.4. Risk assessment

The concentrations of ∑ BTHs, ∑BTRs and ∑BSAs obtained when analysing PM_{coarse} and $PM_{2.5}$ particulate matter air samples from the four sampling sites established in this study were taken into account to estimate the doses of human exposure (ng kg-bw^{-1}day^{-1}) associated with the inhalation of ambient air for people living in the zone under study. As several parameters, including airborne chemical concentrations, frequency and exposure time, average receptor body weight and human breathing rate, can influence average daily doses (ADDs), we applied the mathematical expression described in detail by Asante-Duah et al. (2002) and Maceira et al. (2018). As Table 3 shows, ADDs were assessed for three subpopulations (infants, children and adults) and two exposure scenarios. The geometric mean (low) and the 95th percentile (high) of the concentrations obtained were used to simulate the exposure scenarios. Following USEPA (2000) guidelines, ADDs values for BTHs, BTRs and BSAs found at concentrations lower than the LOD and the LOQ were performed by replacing the concentration values for LOD/2 and LOQ/2, respectively.

As Table 4 shows, ADDs to ∑BTHs were the highest irrespective of the sampling site or particulate matter size, with values ranging from 0.08 to 2.55 ng kg-bw^{-1} day^{-1}. Comparable values of ADDs were also found for ∑BTRs and ∑BSAs, with values ranging from 0.03 to 0.49 ng kg-bw^{-1} day^{-1} and from 0.04 to 0.39 ng kg-bw^{-1} day^{-1}, respectively. In general, the ADDs obtained in this study were of the same order of magnitude as those reported by Maceira et al. (2018) for outdoor air PM$_{10}$ samples from Tarragona, which ranged from 0.06 to 1.08 ng kg-bw^{-1} day^{-1} for ∑BTHs, from 0.28 to 0.99 ng kg-bw^{-1} day^{-1} for ∑BTRs and from 0.014 to 0.15 ng kg-bw^{-1} day^{-1} for ∑BSAs. However, outdoor inhalation is not the major source of human exposure to BTHs, BTRs or BSAs if we compare with the ADDs reported by Wan et al. (2016) and Xu et al. (2017) for indoor air PM$_{10}$ inhalation: from 5.13 to 18.30 ng kg-bw^{-1} day^{-1} for ∑BTHs and from 0.91 to 3.23 ng kg-bw^{-1} day^{-1} for ∑BTRs.

With regard to health risk (HR), few data on safety levels for BTHs, BTRs and BSAs are currently available. For this reason, risk characterization was only considered for BT and BTR. HR (%) calculations were carried out by dividing the average ADDs (ng kg-bw^{-1}day^{-1}) by a reference dose of tolerable daily intake (RfD, ng kg-bw^{-1}day^{-1}) multiplied by 100 (Maceira et al., 2018; Trabalón et al., 2017). Considering an uncertainly factor of 1000 as safety margin, RfD values were obtained by dividing the non-observed adverse effect levels (NOAELs) by 1000 (EC, 2003). The NOAEL values applied for BT and BTR were 5.1 mg kg bw^{-1} day^{-1} (Ginsberg et al., 2011) and 295 mg kg bw^{-1} day^{-1} (Ginsberg et al., 2011), respectively (Schriks et al., 2010). The RfD values were 5100 ng kg-bw^{-1} day^{-1} for BT and as much as 295000 ng kg-bw^{-1} day^{-1} for BTR.

Total HR (HR$_{(BT+BTR)}$) (see Fig. 3) was calculated for the two exposure scenarios and three age groups. For the low-exposure scenario, HR$_{(BT+BTR)}$ ranged from 1.91x10^{-4} to 9.96x10^{-4} for infants and children and from $1.45x10^{-4}$ to $7.45x10^{-4}$ for adults. For the worst exposure scenario, the $HR_{(BT+BTR)}$ ranged from $2.37x10^{-3}$ to $1.70x10^{-2}$ for infants and children and from $1.80x10^{-3}$ to $1.27x10^{-2}$ for adults. Following the trend observed for both concentrations and the ADDs, the $HR_{(BT+BTR)}$ values obtained for PMc_{oarse} samples were higher than those for $PM_{2.5}$ samples. Moreover, if we look at the individual HR in Table 2S, it was found that the HR_{BT} are two orders of magnitude higher than HR_{BTR} and, therefore, the $HR_{(BT+BTR)}$ were conditioned by the HR_{BT} values. Our HR_{BT} results are in agreement with those reported by Maceira et al. (2018) for PM_{10} outdoor air samples from Tarragona, which ranged from $4.60x10^{-4}$ to $3.00x10^{-3}$ for the worst-case scenario. However, the $HR_{(BT+BTR)}$ linked to the inhalation of the compounds under study were much lower than those reported by Trabalón et al. (2017) for the ingestion of fish, with values of up to $1.60x10^{-1}$ - $2.20x10^{-1}$ depending on ages and genders.

4. Conclusions

After monitoring the atmosphere for a year in an area close to the port of Tarragona in order to analyse how the activities carried out there affect air quality, our results showed that, the concentrations of PM_{coarse} and $PM_{2.5}$ did not follow a clear trend since they may be generated by multiple sources, such as activities related to the loading and unloading of goods and road, rail and sea transportation. On the other hand, NO_2 resulting from combustion processes and road traffic was clearly linked to meteorological changes typical of the area under study.

With regard to the concentrations of BTHs, BTRs and BSAs in PM_{coarse} and $PM_{2.5}$ outdoor air samples from the four sampling site, the target compounds found at the highest concentrations were BT, MeBT, ClBT, BTR, 4TTR, MeSBT, 5TTR and BrBSA, with concentrations ranging from <LQM to 17.1 ng m^{-3} regardless of the kind of samples analysed. The other compounds either were not detected or were presented in the samples at concentrations below MQLs. XTR was not detected in any of the samples analysed. Overall, regardless of the kind of sample analysed, BTHs showed the greatest concentration levels, while BSAs were the least detected compounds, with concentrations always below the MQL

except for BrBSA. Our results also showed that the target compounds tend to accumulate in particulate matter of sizes ranging from 2.5 µg m^{-3} to 10 µg m^{-3} (PM_{coarse}) rather than in fine particles ($PM_{2.5}$) and that the concentrations of the target compounds were strictly related to the concentrations of particles.

Because of the presence of these compounds in the particulate matter of outdoor air, ADDs (ng $Kg\text{-}bw^{-1}$ day^{-1}) were calculated for each compounds. Irrespective of the particle size, ADDs ranged from 0.02 to 0.36 ng $Kg\text{-}bw^{-1}$ day^{-1} for the low-case scenario and from 0.08 to 2.55 ng $Kg\text{-}bw^{-1}$ day^{-1} for the high-exposure scenario. These ADDs were much lower than those reported by other authors in the field who analysed, for example, indoor air or dust, so this was not a crucial intake compared to other forms of exposure, such as ingestion, exposure via the dermal route or via inhalation in indoor environments. HR, was calculated only for BT and BTR because of the lack of toxicological information for the other compounds. In the high-exposure scenario, $HR_{(BT+BTR)}$ ranged from $2.37x10^{-3}$ to $1.70x10^{-2}$ for infants and children and from $1.80x10^{-3}$ to $1.27x10^{-2}$ for adults. These results were conditioned for the HR_{BT} values since they were two orders of magnitude higher than for the HR_{BTR} values.

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Figure caption

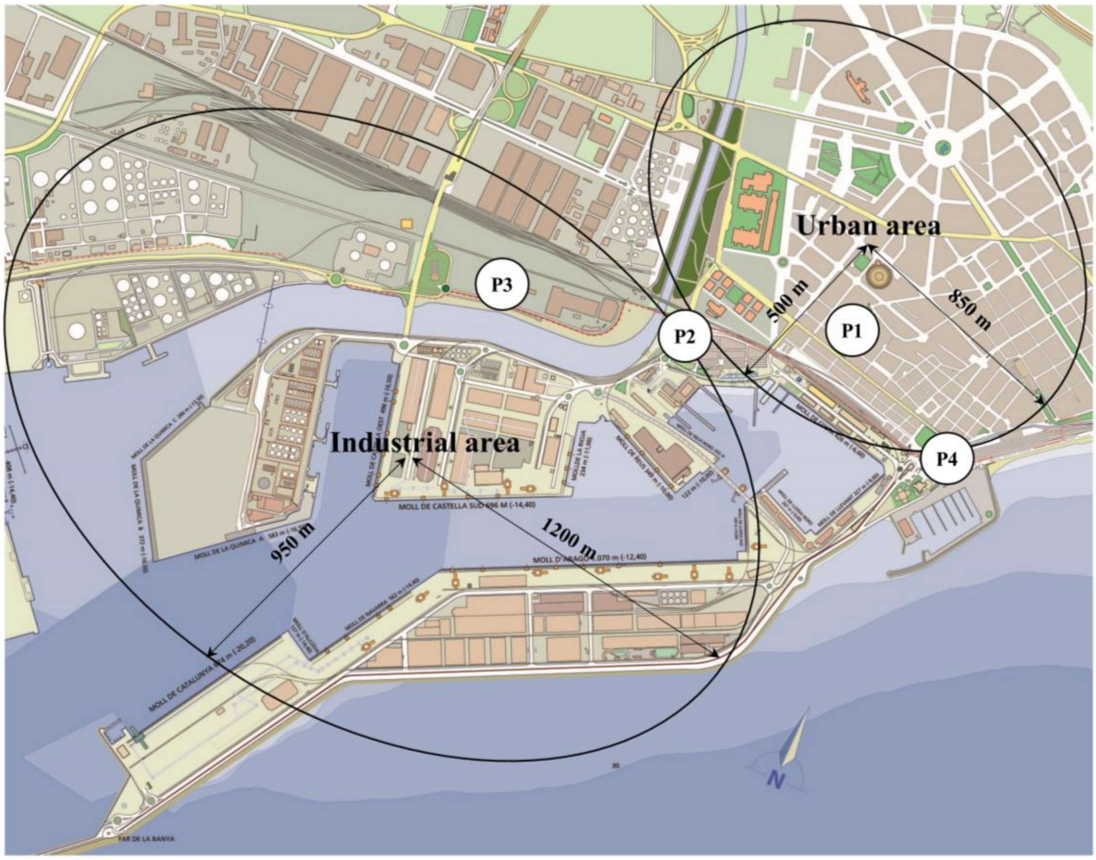

Fig. 1. Map of the city of Tarragona showing the location of the four sampling sites and distance information.

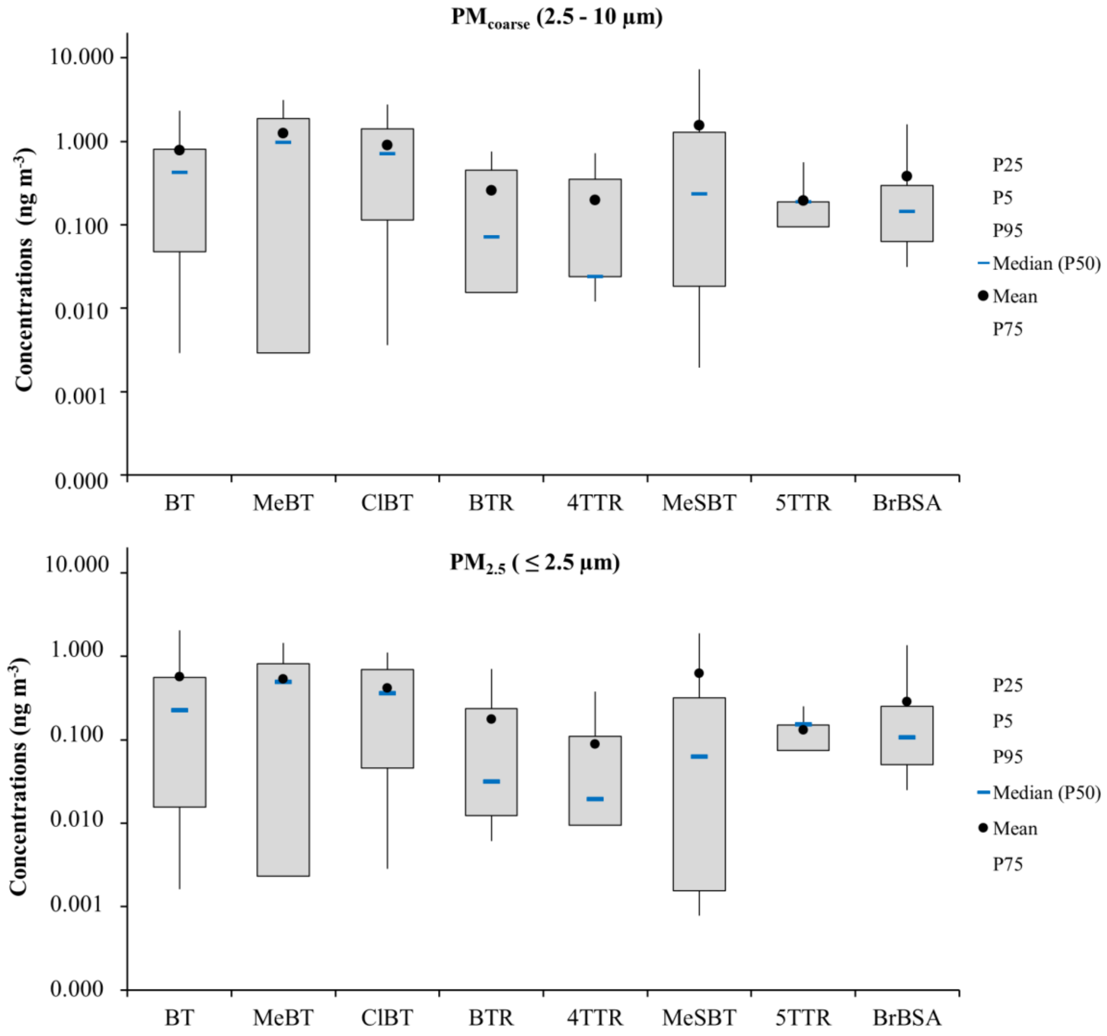

Fig. 2. Percentile distribution of the concentrations of the most representative target compounds found in the outdoor air samples analysed (PM_{coarse} and $PM_{2.5}$). The box plot of for each sampling site represents the 25th and 75th percentiles of the concentrations. The horizontal line inside the box indicates the median for the concentrations. The bottom and top lines indicate the minimum and maximum concentrations. The circle indicates the average concentrations.

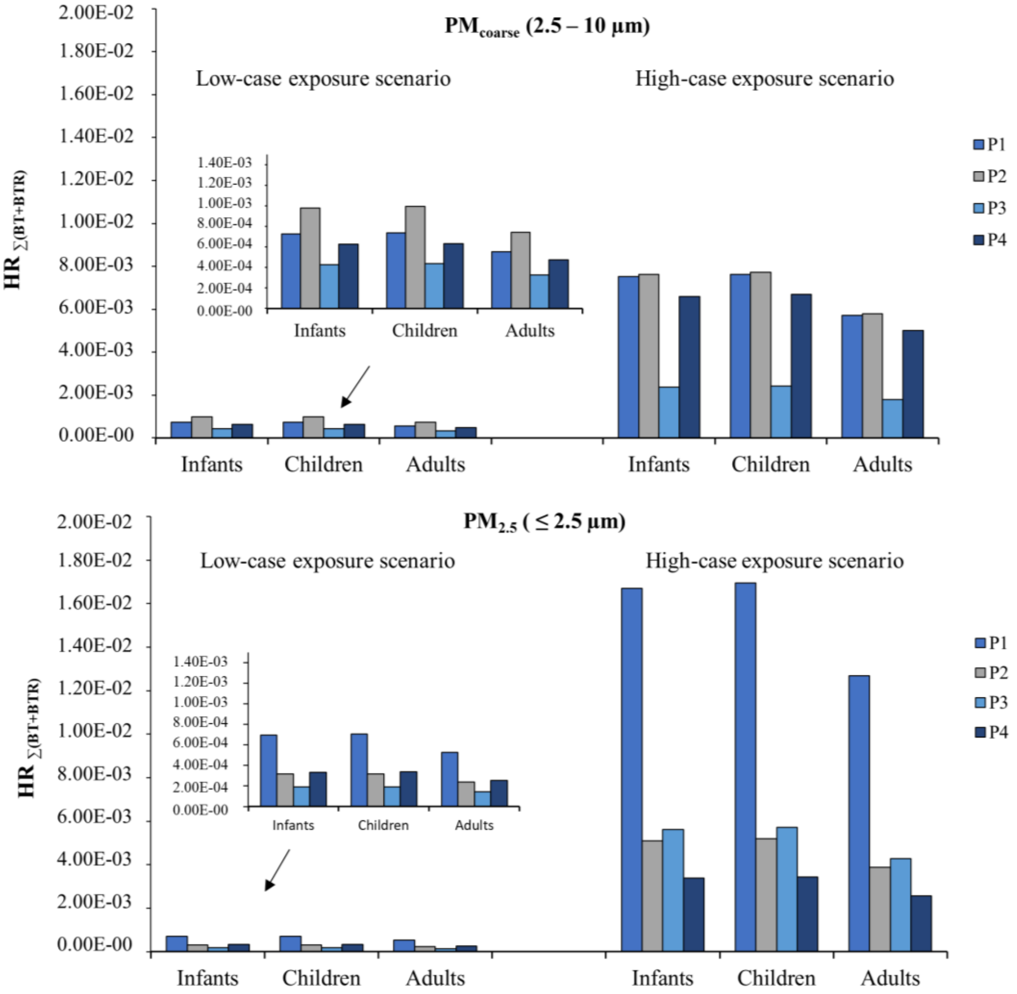

Fig. 3. Total health risk (HR$_{(BT+BTR)}$) in the four sampling sites studied for PM$_{coarse}$ and PM$_{2.5}$ samples, three age groups and two exposure scenarios.

Table 1. Concentrations of the target BTHs, BTRs and BSA in PM_{coarse} samples (ng m^{-3}) from the four sampling sites in the port of Tarragona (*n* = 12 at each sampling site). The concentrations of particles found during the sampling period, expressed as µg m^{-3}, are also included in the table.

Name	**MDLs (ng m^{-3})**	**MQLs (ng m^{-3})**	**Concentrations (ng m^{-3})**							
			P1		**P2**		**P3**		**P4**	
			Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
BT	0.003	0.006	<MQL - 2.27	0.75	<MQL - 8.49	1.29	<MQL - 0.65	0.33	<MQL - 2.53	0.63
MeBT	0.003	0.006	<MQL - 2.32	0.99	<MQL - 9.79	1.76	n.d.- 2.10	0.76	<MQL - 3.99	1.30
ClBT	0.004	0.007	<MQL - 3.14	0.84	<MQL- 2.97	1.05	<MQL - 2.23	0.69	<MQL - 3.51	0.96
BTR	0.014	0.035	n.d. - 1.27	0.30	n.d. - 0.64	0.15	<MQL -0.70	0.27	<MQL - 0.78	0.31
4TTR	0.021	0.049	n.d. - 1.05	0.23	n.d. - 0.76	0.20	n.d. - 0.64	0.16	n.d. - 0.77	0.20
MeSBT	0.002	0.004	<MQL - 3.94	1.04	<MQL -17.05	2.54	n.d. -2.64	0.41	<MQL - 12.13	1.80
5TTR	0.139	0.347	n.d. - 0.92	0.27	n.d. - 0.44	0.17	n.d. - <MQL	0.14	n.d. - 0.82	<MQL
BSA	0.003	0.006	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL
NH_2BT	0.021	0.049	n.d. - 0.15	<MQL	n.d. - 0.31	<MQL	n.d. - 0.12	<MQL	-	n.d.
o-TSA	0.002	0.003	n.d. - <MQL	<MQL	n.d.	n.d.	-	n.d.	-	n.d.
p-TSA	0.062	0.139	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL
OHBT	0.004	0.007	n.d. - 0.16	0.03	n.d. - 0.16	0.02	n.d. - 0.38	0.075	n.d. - 0.20	0.03
Et-p-TSA	0.021	0.049	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	-	n.d.	-	n.d.
Me-p-TSA	0.014	0.035	n.d. - <MQL	<MQL	-	n.d.	-	n.d.	-	n.d.
XTR	0.014	0.035	-	n.d.	-	n.d.	-	n.d.	-	n.d.
BrBSA	0.062	0.139	n.d. - 1.59	0.29	n.d. - 2.67	0.47	<MQL - 1.19	0.25	n.d. - 1.87	0.46
	∑ BTHs		0.09 - 9.62	3.65	0.15 - 13.45	4.10	0.13 - 4.86	2.27	0.01 - 20.50	4.71
	∑ BTRs		<MQL - 3.17	0.78	n.d. -1.21	0.49	0.20 - 1.01	0.50	<MQL - 1.46	0.66
	∑ BSAs		n.d. - 1.59	0.31	n.d. - 2.67	0.49	<MQL - 1.19	0.28	<MQL - 1.87	0.47
	∑ (BTHs + BTRs + BSAs)		0.44 - 11.67	4.75	0.60 - 14.97	5.08	1.01 - 5.47	3.05	1.59 - 21.72	5.84
	Particles (µg m^{-3})		1.66 - 49.86	11.00	1.15 - 64.81	11.77	0.17 - 39.8	9.40	0.85 - 51.05	13.44

Table 2. Concentrations of the target BTHs, BTRs and BSA in $PM_{2.5}$ samples (ng m^{-3}) from the four sampling sites placed in the port of Tarragona. (*n* = 12 at each sampling site). The concentrations of particles found during the sampling period, expressed as µg m^{-3}, are included in the table.

Name	**MDLs (ng m^{-3})**	**MQLs (ng m^{-3})**	**Concentrations (ng m^{-3})**							
			P1		**P2**		**P3**		**P4**	
			Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
BT	0.002	0.003	<MQL - 7.33	1.13	<MQL - 2.16	0.46	<MQL - 2.20	0.37	<MQL - 1.25	0.32
MeBT	0.002	0.003	<MQL - 1.85	0.71	<MQL - 1.81	0.57	<MQL - 1.12	0.35	<MQL - 1.39	0.45
ClBT	0.002	0.004	0.01 - 1.15	0.46	<MQL - 1.13	0.47	<MQL - 1.02	0.30	<MQL - 1.24	0.39
BTR	0.008	0.019	n.d. - 1.20	0.20	n.d. - 1.06	0.17	n.d. - 0.38	0.11	n.d. - 0.75	0.20
4TTR	0.012	0.027	n.d. - 0.18	<MQL	n.d. - 0.39	0.09	n.d. - 0.33	0.07	n.d. - 0.63	0.14
MeSBT	0.001	0.002	n.d. - 2.08	0.28	n.d. - 5.64	0.61	n.d. - 0.62	0.09	n.d. - 10.77	1.26
5TTR	0.077	0.193	n.d. - 0.34	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - 0.48	<MQL
BSA	0.002	0.003	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL
NH_2BT	0.012	0.027	n.d. - <MQL	<MQL	n.d. - 0.32	0.05	n.d. - 0.08	<MQL	n.d. - 0.07	<MQL
o-TSA	0.001	0.002	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	-	n.d.	-	n.d.
p-TSA	0.035	0.077	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL
OHBT	0.002	0.004	n.d. - 0.09	0.02	n.d. - 0.07	0.02	n.d. - 0.07	0.01	n.d. - 0.11	0.02
Et-p-TSA	0.012	0.027	n.d. - <MQL	<MQL	n.d. - <MQL	<MQL	-	n.d.	-	n.d.
Me-p-TSA	0.008	0.019	n.d. - <MQL	<MQL	-	n.d.	-	n.d.	-	n.d.
XTR	0.008	0.019	-	n.d.	-	n.d.	-	n.d.	-	n.d.
BrBSA	0.035	0.077	n.d. - 0.72	0.15	n.d. - 1.45	0.36	<MQL - 1.49	0.39	<MQL - 1.06	0.24
	∑ BTHs		0.05 - 8.45	2.60	0.01 - 10.59	2.16	0.06 - 2.67	1.13	0.08 - 14.29	2.43
	∑ BTRs		n.d. - 1.32	0.26	<MQL - 1.44	0.35	n.d. - 0.73	0.28	n.d. - 1.52	0.49
	∑ BSAs		n.d. - 0.72	0.15	n.d. - 1.45	0.37	<MQL - 1.49	0.41	<MQL - 1.06	0.27
	∑ (BTHs + BTRs + BSAs)		0.50 - 8.67	3.00	0.47 - 12.29	2.88	0.91 - 2.96	1.83	0.62 - 14.67	3.19
	Particles (µg m^{-3})		1.07 - 16.22	6.98	0.51 - 53.50	7.81	1.82 - 45.85	6.42	1.54 - 20.74	8.01

Table 3. Average daily dose (ADD, ng kg-bw^{-1} day^{-1}) of ∑BTHs, ∑BTRs and ∑BSAs through inhalation of ambient air particulate matter (PM_{coarse} and $PM_{2.5}$) at the four sampling sites for three age groups and two exposure scenarios.

		ADD (ng kg-bw^{-1} day^{-1})											
		PM_{coarse}						**$PM_{2.5}$**					
		Low-case scenario			**High-case scenario**			**Low-case scenario**			**High-case scenario**		
		Infants	**Children**	**Adults**	**Infants**	**Children**	**Adults**	**Infants**	**Children**	**Adults**	**Infants**	**Children**	**Adults**
P1	∑BTHs	0.322	0.327	0.244	1.624	1.649	1.233	0.240	0.243	0.182	1.393	1.415	1.057
	∑BTRs	0.090	0.091	0.068	0.481	0.488	0.365	0.037	0.037	0.028	0.193	0.196	0.146
	∑BSAs	0.039	0.040	0.030	0.247	0.251	0.188	0.027	0.027	0.020	0.102	0.103	0.077
P2	∑BTHs	0.356	0.361	0.270	2.005	2.036	1.522	0.158	0.160	0.120	1.198	1.217	0.909
	∑BTRs	0.073	0.074	0.055	0.223	0.226	0.169	0.051	0.052	0.039	0.197	0.200	0.150
	∑BSAs	0.057	0.058	0.043	0.384	0.390	0.292	0.047	0.048	0.036	0.272	0.276	0.206
P3	∑BTHs	0.226	0.230	0.172	0.885	0.898	0.672	0.102	0.104	0.077	0.468	0.476	0.355
	∑BTRs	0.092	0.093	0.070	0.203	0.207	0.154	0.045	0.046	0.034	0.131	0.133	0.099
	∑BSAs	0.044	0.045	0.033	0.167	0.170	0.127	0.044	0.044	0.033	0.278	0.282	0.211
P4	∑BTHs	0.309	0.313	0.234	2.508	2.546	1.903	0.185	0.188	0.140	1.467	1.490	1.114
	∑BTRs	0.099	0.100	0.075	0.275	0.279	0.209	0.067	0.068	0.050	0.277	0.281	0.210
	∑BSAs	0.062	0.063	0.047	0.332	0.337	0.252	0.041	0.041	0.031	0.185	0.188	0.140

SUPPLEMENTARY MATERIAL

Table 1S. Target compounds in chromatographic elution order, retention times, quantifier and qualifier ions, instrumental detection (LOD) and quantification (LOQ) limits and intra-day and inter-day repeatabilities (*n* = 5, 0.5 ng µL^{-1}). Extraction recoveries for PM_{coarse} and $PM_{2.5}$ filters are included in the table (*n* = 5, 0.5 ng µL^{-1}).

Nº	**Name**	**Retention time (t_R, min)**	**Qualifier and quantifier ions [*] (m/z)**	**LOD (ng)**	**LOQ (ng)**	**Intra-day repeatability (RSD%)**	**Inter-day repeatability (RSD%)**	**Recoveries [**]**	
								PM_{coarse}	**$PM_{2.5}$**
IS	d4-BT	5.71	**139 (100 %)** 112 (26 %) 70 (16 %)	-	-	-	-	-	-
1	BT	5.73	**135 (100 %)** 108 (25 %) 69 (12 %)	0.002	0.004	2.1	3.7	93 (3.5)	95 (3.9)
2	MeBT	6.16	**149 (100 %)** 148 (26 %) 108 (40 %) 69 (20 %)	0.002	0.004	1.8	2.9	89 (2.8)	87 (3.3)
3	ClBT	6.56	171 (38 %) **169 (100 %)** 134 (27 %) 108 (54 %)	0.003	0.005	2.3	3.0	82 (3.7)	84 (4.0)
IS	d4-BTR	8.36	**123 (100 %)** 95 (85 %) 67 (39 %)	-	-	-	-	-	-
4	BTR	8.46	**119 (100 %)** 91 (67 %) 64 (63 %)	0.010	0.025	3.1	4.3	89 (3.4)	91 (3.7)
5	4TTR	8.80	133 (82 %) **104 (100 %)** 77 (41 %)	0.015	0.035	2.8	4.4	90 (3.1)	93 (3.2)
6	MeSBT	9.10	**181 (100 %)** 148 (85 %) 108 (49 %)	0.001	0.003	3.4	4.9	97 (3.9)	94 (4.1)
7	5TTR	9.16	133 (77 %) **104 (100 %)** 77 (40 %)	0.100	0.250	4.1	5.2	85 (5.1)	87 (4.7)
8	BSA	9.44	157(25 %) 141 (21 %) 93 (31 %) **77 (100 %)**	0.002	0.004	3.5	4.2	88 (4.7)	90 (5.0)
9	NH_2BT	9.62	**150 (100 %)** 123 (33 %) 96 (31 %)	0.015	0.035	2.8	3.8	92 (4.7)	89 (4.5)
10	*o*-TSA	9.96	106 (90 %) 91 (72 %) **90 (100 %)** 65 (40 %)	0.001	0.002	3.9	4.7	95 (5.3)	97 (5.1)
IS	d4-*p*-TSA	10.31	175 (51 %) 159 (40 %) **95 (100 %)**	-	-	-	-	-	-
11	*p*-TSA	10.33	185 (19%) 155 (17%) **91 (100 %)** 65 (25%)	0.045	0.100	1.9	2.9	93 (4.4)	90 (4.7)
12	OHBT	10.35	**151 (100 %)** 123 (82%) 96 (73%)	0.003	0.005	2.7	3.6	94 (4.6)	91 (4.2)
13	Et-*p*-TSA	10.37	184 (19%) 155 (47%) **91 (100 %)** 65 (28%)	0.015	0.035	3.3	4.5	89 (5.4)	92 (4.8)
14	Me-*p*-TSA	10.38	171 (27%) 155 (26%) **91 (100 %)** 65 (32%)	0.010	0.025	2.7	3.9	87 (4.6)	88 (3.8)
15	XTR	10.44	147 (59%) **118 (100 %)** 91 (50%)	0.010	0.025	2.9	4.1	85 (5.1)	87 (4.7)
16	BrBSA	12.18	237 (58%) 157 (82%) 155 (90%) **75 (100 %)**	0.045	0.100	3.8	5.4	88 (5.7)	90 (5.2)

IS = Internal standard.

[**] Relative standard deviation (%) in brackets.

[*] Quantifier ions are shown in bold type. In brackets are the relative abundance percentage of each ion.

Table 2S. Average health risk (HR, %) of BT and BTR through inhalation of ambient air particulate matter (PM_{coarse} and $PM_{2.5}$) at the four sampling sites for three age groups and two scenarios.

		HR (%)											
		PM_{coarse}						**$PM_{2.5}$**					
		Low scenario			**High scenario**			**Low scenario**			**High scenario**		
		Infants	**Children**	**Adults**	**Infants**	**Children**	**Adults**	**Infants**	**Children**	**Adults**	**Infants**	**Children**	**Adults**
P1	**BT**	7.22E-04	7.33E-04	5.48E-04	7.44E-03	7.56E-03	5.65E-03	6.94E-04	7.04E-04	5.26E-04	1.67E-02	1.69E-02	1.26E-02
	BTR	4.63E-06	4.70E-06	3.51E-06	7.81E-05	7.93E-05	5.93E-05	2.56E-06	2.60E-06	1.94E-06	4.45E-05	4.52E-05	3.38E-05
	∑(BT+BTR)	7.27E-04	7.38E-04	5.52E-04	7.52E-03	7.64E-03	5.71E-03	6.96E-04	7.07E-04	5.28E-04	1.67E-02	1.70E-02	1.27E-02
P2	**BT**	9.79E-04	9.93E-04	7.43E-04	7.58E-03	7.70E-03	5.75E-03	3.13E-04	3.18E-04	2.38E-04	5.06E-03	5.14E-03	3.84E-03
	BTR	2.86E-06	2.90E-06	2.17E-06	3.54E-05	3.59E-05	2.69E-05	2.56E-06	2.60E-06	1.95E-06	4.56E-05	4.63E-05	3.46E-05
	∑(BT+BTR)	9.81E-04	9.96E-04	7.45E-04	7.62E-03	7.73E-03	5.78E-03	3.16E-04	3.21E-04	2.40E-04	5.11E-03	5.19E-03	3.88E-03
P3	**BT**	4.22E-04	4.28E-04	3.20E-04	2.34E-03	2.37E-03	1.77E-03	1.89E-04	1.92E-04	1.43E-04	5.60E-03	5.69E-03	4.25E-03
	BTR	7.49E-06	7.61E-06	5.69E-06	3.87E-05	3.93E-05	2.94E-05	1.90E-06	1.93E-06	1.44E-06	2.25E-05	2.28E-05	1.71E-05
	∑(BT+BTR)	4.30E-04	4.36E-04	3.26E-04	2.37E-03	2.41E-03	1.80E-03	1.91E-04	1.94E-04	1.45E-04	5.63E-03	5.71E-03	4.27E-03
P4	**BT**	6.19E-04	6.28E-04	4.70E-04	6.56E-03	6.66E-03	4.98E-03	3.29E-04	3.34E-04	2.50E-04	3.34E-03	3.39E-03	2.53E-03
	BTR	7.33E-06	7.44E-06	5.56E-06	4.62E-05	4.69E-05	3.51E-05	4.07E-06	4.13E-06	3.09E-06	4.08E-05	4.15E-05	3.10E-05
	∑(BT+BTR)	6.26E-04	6.36E-04	4.75E-04	6.60E-03	6.71E-03	5.01E-03	3.33E-04	3.38E-04	2.53E-04	3.38E-03	3.43E-03	2.56E-03

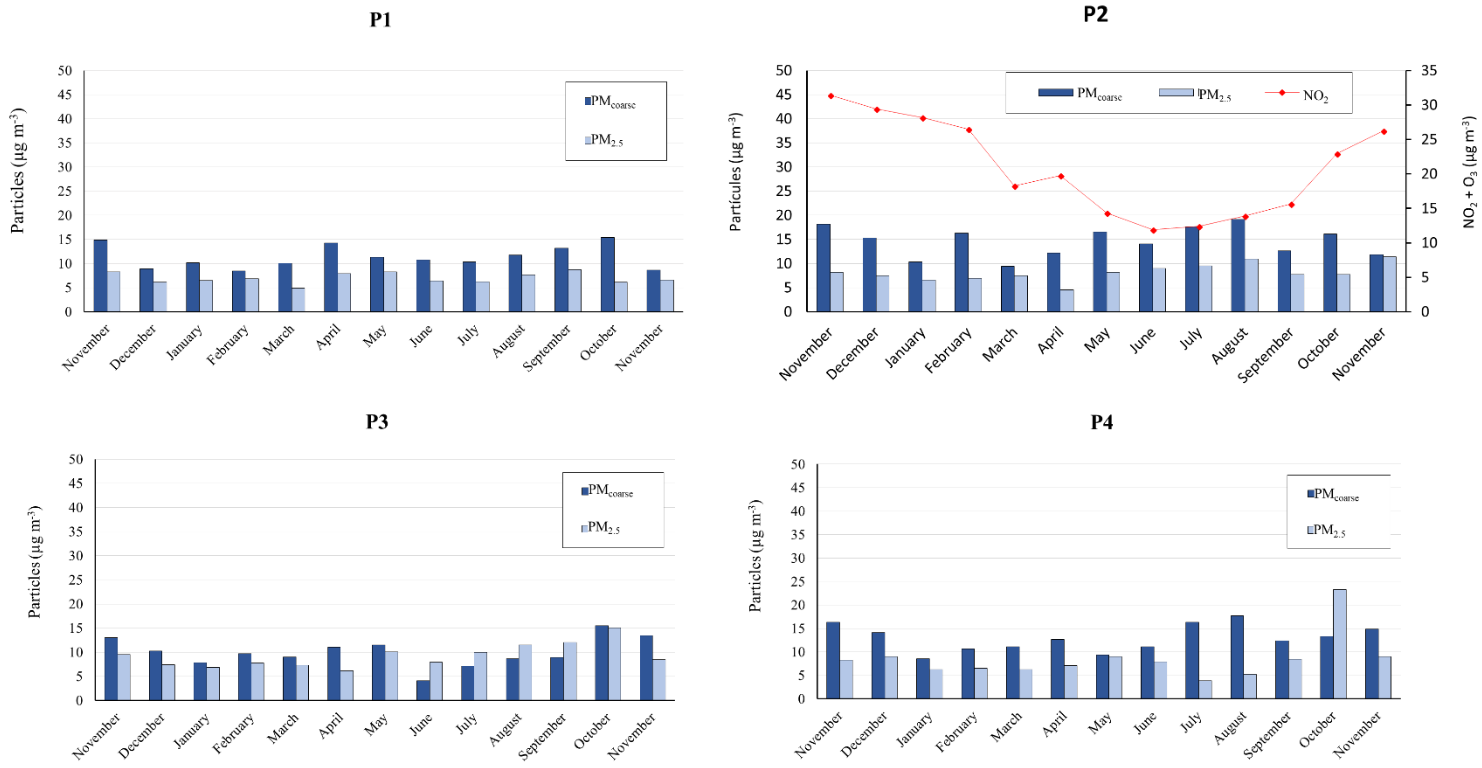

Fig. 1S. Column graphs showing the evolution of PM_{coarse} and $PM_{2.5}$ values throughout the one-year period. NO_2 and O_3 concentrations at site 2 (P2) are also shown.

Fig. 2S. Bar chart showing the sum of the average concentrations of BTHs, BTRs and BSAs (ng m^{-3}) found when analysing PM_{coarse} and $PM_{2.5}$ outdoor air samples from the sampling sites at the port of Tarragona. The average concentration of particle expressed as µg m^{-3} were also added (red line).