# Benzotriazoles, Benzothiazoles and Trace Elements in an Urban Road Setting in Trondheim, Norway: Re-Visiting the Chemical Markers of Traffic Pollution

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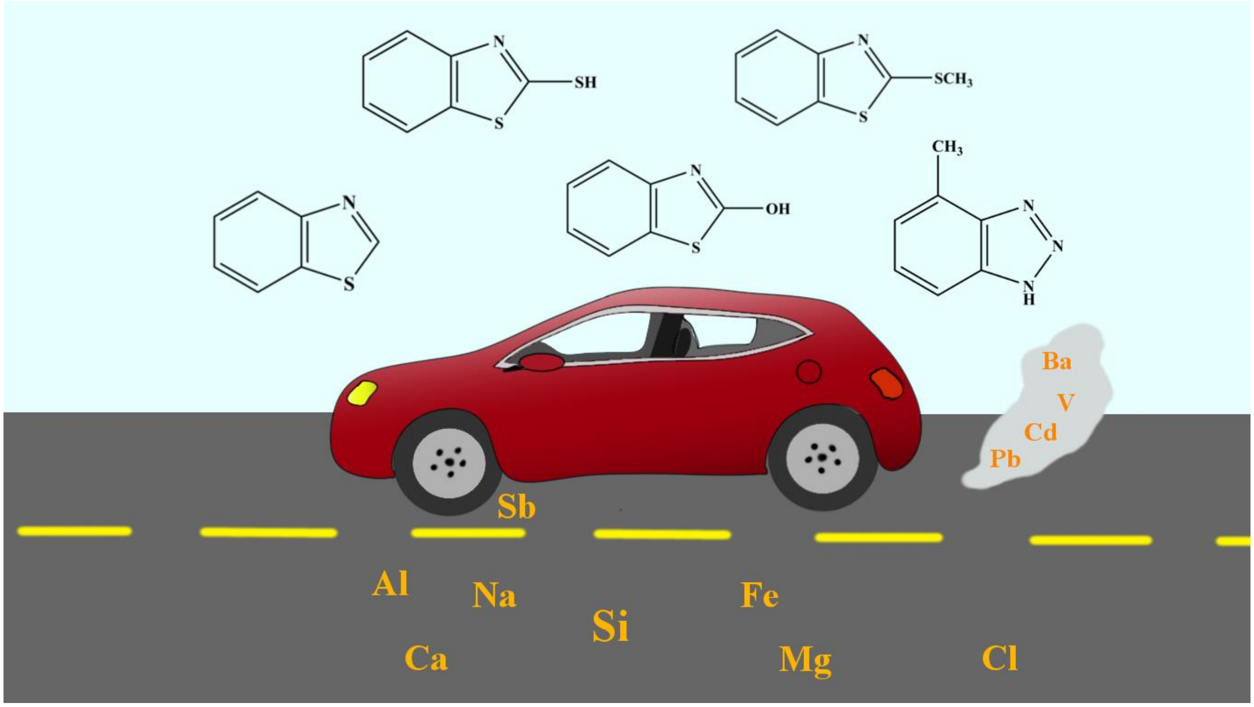

Graphical Abstract

## HIGHLIGHTS

- 79 chemicals were determined in a heavily trafficked urban road setting;
- Concentrations between the studded and the non-studded tire season were presented;
- New chemical markers of metal corrosion, and tire tear or wear were proposed;
- Benzotriazole-5-carboxyl acid was reported in the relevant environmental matrices;
- Estimated daily intakes were calculated based on airborne particulate matter levels.

# ABSTRACT

Road traffic emissions are known to contribute heavily to the pollution in urban environments. The aim of this study was to establish specific traffic pollution markers in an urban road setting based on the occurrence profiles of benzotriazoles, benzothiazoles and trace elements in road dust and relevant matrices, including airborne particulate matter and core asphalt. Benzotriazoles and benzothiazoles are high-production volume chemicals that are used as complexing and anticorrosive agents for metals, act as vulcanizing accelerators for rubber materials, and possess anti-freezing/anti-icing properties. In this study, six benzothiazoles (benzothiazole, 2-morpholin-4-yl-benzothiazole, 2-hydroxy-benzothiazole, 2-thio-benzothiazole, 2-methylthio-benzothiazole, and 2-amino-benzothiazole), seven benzotriazoles (1H-benzotriazole, 1-hydroxy-benzotriazole, 5-chloro-1H-benzotriazole, tolyltriazole, xylyltriazole, benzotriazole-5-carboxyl acid, and 5-amino-1H-benzotriazole), and 66 trace elements were determined in road dust samples from a sub-arctic urban road setting in Norway, and seasonal occurrence profiles were assessed between the studded and the non-studded tire season. The road dust was collected as suspended particulate matter in an aqueous phase with the introduced dust sampler in Scandinavia, the *Wet Dust Sampler*. The concentrations of the sum of seven benzotriazoles (Σ(7)BTRs) and six benzothiazoles (Σ(6)BTHs) in road dust ranged from 191 to 3054 ng/L and 93.4 to 1903 ng/L, respectively. To the best of our knowledge, 1H-benzotriazole and tolyltriazole are reported for the first time as suitable markers of metal corrosion in vehicles. From the benzothiazole class, 2-thio-benzothiazole was found to be a suitable marker of tire rubber particles, while its methylated derivative, 2-methylthio-benzothiazole, was found to be a marker of chemical leaching. In addition, different types of new unused tires (summer, studded, and non-studded) were analyzed to assess their benzothiazoles and benzotriazoles content. Based on the concentrations found for benzotriazoles and benzothiazoles in airborne particulate matter, human exposure doses were calculated, and the estimated daily intake doses were found on the order of picograms per day.

## KEYWORDS

Benzotriazoles, Benzothiazoles, Metals, Dust, Markers, Pollution

## ABBREVIATIONS

Benzothiazoles, BTHs; 2-mercaptobenzothiazole, 2-S-BTH; benzothiazole, BTH; 2-hydroxy-benzothiazole, 2-OH-BTH; 2-morpholin-4-yl-benzothiazole, 2-M-BTH; 2-methylthio-benzothiazole, 2-Me-S-BTH; 2-aminobenzothiazole, 2-ABTH; benzotriazoles, BTRs; 1H-benzotriazole, BTR; tolyltriazole, TTR; 1-hydroxy-benzotriazole, 1-OH-BTR; benzotriazole-5-carboxyl acid, BTR-COOH; 5-chloro-1H-benzotriazole, 5-Cl-BTR; xylyltriazole, XTR; 5-amino-1H-benzotriazole, 5-ABTR;  Lower Limit of Quantification, LLOQ; Limit of Detection, LOD; Relative Standard Deviation, R.S.D.; Wet Dust Sampler, WDS; Particulate Matter, PM; Quality Assurance/Quality Control, (QA/QC); High Density Polyethylene, HDPE; Airborne Particulate Matter, APM.

## 1. Introduction

The emissions of organic and inorganic chemicals from road traffic activity are established as the main source of pollution in an urbanized road setting **(Klint, 2001; Markiewicz et al., 2017; Pant and Harrison, 2013)**. All vehicle tires contain a multitude of chemicals that are of potential concern since a broad spectrum of those are released into the environment as they wear and tear **(Rogge et al., 1993)**. Thus, tire debris are significant sources of Zn, Mn, Fe, Co, Ni, Cu, Cd, and Pb **(Thorpe and Harrison, 2008)**. It is documented that tire threads contain a high concentration of Zn since ZnO is added as a vulcanization activator during the manufacturing process of tires **(Fukuzaki et al.; 1986)**. In addition, benzothiazoles (BTHs) are organic chemicals that also derive from tires (which account for 2/3 of the total rubber production) and their widespread occurrence in the environment is well-documented **(Liao et al., 2018)**. Of these, 2-mercaptobenzothiazole (2-S-BTH) is the main vulcanization accelerator used **(Herrero et al., 2014; Leng and Gries, 2017)**, while benzothiazole (BTH) and 2-hydroxy-benzothiazole (2-OH-BTH) are common breakdown products of vulcanizing agents and antioxidants added to the rubber materials during manufacturing **(Reddy and Quinn, 1997)**. Moreover, 2-morpholin-4-yl-benzothiazole (2-M-BTH) is documented as an impurity in rubber **(Reddy and Quinn, 1997)**, 2-methylthio-benzothiazole (2-Me-S-BTH) is a major methylation product of 2-S-BTH **(De Wever and Verachtert, 1997)** and 2-aminobenzothiazole (2-ABTH) has been widely used as a structural unit in the synthesis of antioxidants and thermoplastic polymers **(Sun et al., 2012)**. BTHs are also used as corrosion inhibitors of metal surfaces and antifreeze agents in fluid systems of vehicles **(Asimakopoulos et al., 2013a)**. Benzotriazoles (BTRs) are another class of organic compounds that are used as corrosion inhibitors for metal alloys and found widespread in environmental media **(Agafonkina et al., 2012; Breedveld et al., 2003; Cantwell et al., 2015; Downs, 1986; Felis et**

**al., 2016; Huntscha et al., 2014; Molloy and Partch, 2013; Park and Bell, 1984)**. Of these, 1H-benzotriazole (BTR) and tolyltriazole (TTR) are used as corrosion inhibitors for copper and brass (alloy of Cu and Zn) **(Cantwell et al., 2015)**, and it is reported that they are transformed aerobically to 1-hydroxybenzotriazole (1-OH-BTR) and benzotriazole-5-carboxyl acid (BTR-COOH), respectively **(Felis et al., 2016; Huntscha et al., 2014)**. Other BTR derivatives such as 5-chloro-1H-benzotriazole (5-Cl-BTR) and xylyltriazole (XTR or 5,6-dimethyl-1H-benzotriazole) are also used as corrosion inhibitors **(Agafonkina et al., 2012; Huntscha et al., 2014; Molloy and Partch, 2013)**, while 5-amino-1H-benzotriazole (5-ABTR) is applied for enhanced durability of adhesive copper/epoxy joints **(Park and Bell, 1984)**.

In 2008, the *Swedish National Road and Transport Research Institute* introduced the Wet Dust Sampler (WDS), a device for sampling particulate matter (PM) from road surfaces, regardless of particle size, with pressurized deionized water **(Jonsson et al., 2008)**. The WDS is effective in collecting particulates, since it can collect 95 % of the PM according to performance tests **(Jonsson et al., 2008)**. Currently, a limited number of WDS prototypes are distributed in Scandinavia, and Norway possess one prototype located at the Norwegian Public Roads Administration in Trondheim, Norway.

In this study, road dust samples were collected with the WDS from a central heavily trafficked urban road at Elgeseter street in Trondheim, Norway, with the objectives of establishing concentrations and profiles of 6 BTHs, 7 BTRs and 66 elements, and evaluate seasonal variations between the studded and the non-studded tire season. To the best of our knowledge, this is the first time that distribution coefficients ($K_d$ values; L kg$^{-1}$) were estimated in WDS-samples, and that BTR-COOH was documented in road dust and relevant environmental matrices. Studded tires are been used in Nordic countries for road safety purposes but are considered to have greater environmental impacts than the non-studded due to their significantly higher contribution to road wear and emissions of particles **(Gustafsson and Eriksson, 2015)**. Thus, new unused summer, studded, and non-studded (winter) vehicle tires were analyzed to assess their BTHs and BTRs content. In addition, core asphalt, bitumen, and airborne particulate matter (APM) sample(s) were also collected from the urban road setting to investigate occurrence profiles and estimate human daily intakes (EDIs) of BTHs and BTRs. This is the first study to establish traffic pollution markers in an urban road setting based on concentration profiles of BTHs, BTRs, and trace elements.

## 2. Materials and methods

### 2.1. Chemicals and Materials

Multielement stock solutions (*Elemental Scientific*, *Omaha*, *NE, U.S.*) that contained 66 elements, including, Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Pt, Rb, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr were obtained. Two custom made sets of calibration solutions (CS; *Elemental Scientific, Omaha, NE, U.S.*) were obtained for ICP-MS analysis from two independent producers. One of the sets was used as a CS and the other for quality assurance/quality control (QA/QC). Standards of BTH (≥ 97%), BTR (≥ 98%), XTR (≥ 99%), TTR (4-methyl-1H-benzotriazole isomer; ≥ 90%), BTR-COOH (99%), 5-Cl-BTR (99%), 5-ABTR (Aldrich$^{CPR}$ grade), 2-S-BTH (97%), 2-OH-BTH (98%), 2-ABTH (97%), 2-Me-S-BTH (97%), 2-M-BTH (CPR), 1-OH-BTR (≥ 97%) and BTR-$^2d_4$ (10 µg/mL in acetone) were purchased from *Sigma-Aldrich (Steinheim, Germany)*. Methanol (MeOH) and acetonitrile (ACN) of LC-MS grade, and dichloromethane (DCM) of analytical grade were obtained from *Merck (Darmstadt, Germany)*. Formic acid (98% v/v), hydrochloric acid (HCl), and ammonium hydroxide were obtained from *Sigma-Aldrich (Steinheim, Germany)*. Concentrated nitric acid (UltraPure grade) was obtained by distillation with *Milestone SubPur (Sorisole, BG, Italy)*. Water was purified with a Milli-Q grade water purification system (*Q-option, Elga Labwater, Veolia Water Systems LTD, UK*). Further detailed information concerning standard stock solutions and other materials are presented in the *Supplementary data*.

## 2.2. Sample Collection

The road dust, core asphalt and APM samples were collected from the urban road setting at Elgeseter street in Trondheim, Norway [63°25'10.5"N, 10°23'45.2"E; sub-Arctic region] during 2017. Elgeseter street is a heavily trafficked road with a daily average passing of 30.000 motor vehicles.

For the collection of road dust samples, two sampling campaigns were performed on two different days on the same sampling site; on the 2nd of October that corresponds to the non-studded tire season, and on the 23rd of November that corresponds to the studded tire season. These dates were selected because the use of studded tires in Norway is strictly regulated by law from the beginning of November to mid-April**,** while there are no limitations on the use of non-studded (winter) tires **(NRD, 2014)**. In each of the two campaigns, 16 road dust samples were consecutively collected from the same 15 m road stretch (1 sample per meter) near the pavement edge. The collected road dust sample from the WDS consists of suspended particulate matter in an aqueous phase, and therefore in this work referred to as "WDS-sample". The samples were collected in plastic bottles (high density polyethylene; HDPE) with a sample volume of approximately 2.1 L per sample, and stored in the dark at 4°C.

Core asphalt columns with diameter of 10 cm and height of 50 cm were drilled out from the road. The top layer of each core sample (3 cm) was obtained and stored in a water bath (at 4-5 °C). The cold-water bath simulates the saturated road conditions (raining conditions) that are common in Norway and known to increase asphalt weathering **(Klint, 2001)**. These core asphalt samples were collected during the non-studded tire season to be subjected to the *Asphalt Prall Test (see Supplementary data)* **(Snilsberg et al., 2008)**. The suspended asphalt particles that were produced for every core asphalt sample by this process, were washed out and collected into HDPE plastic bottles **(Snilsberg et al., 2008)**; in this work referred to as “Prall-sample”.

Fifty mL of the WDS- and Prall-samples were immediately filtered after collection for organic analysis. The particulate matter derived from filtration was dried in the fume hood at room temperature (20 °C) for 72-h, weighed, and thereafter stored at −20 °C until analysis. The obtained weight/amount of particulate matter was ~3.5-fold higher in the WDS-samples in the studded (median: 80.3 mg) than the non-studded season (median: 23.2 mg); more road dust is generated during the winter season **(Pant and Harrison, 2013)**. The filtered dissolved phase of WDS- and Prall-samples were stored in the dark at 4 °C until analysis.

APM samples were collected during two consecutive sampling periods with the instrumentation described in the *Supplementary data*. The first set of air filters was installed on the 9th of September, and the duration of the sampling was 10 days. The set was retrieved on the 19th of September, and thereafter, the second set of filters was installed. The duration of the second sampling period was 14 days, and the filters were retrieved on the 2nd of October. In each sampling campaign, 4 different APM filters (samples) were retrieved: $PM_{2.5}$, $PM_{2.5\text{-}10}$, volatile $PM_{2.5}$, and volatile $PM_{2.5\text{-}10}$; and stored in the dark at -20 °C. During the sampling periods, the volatile PMs were kept at 4°C, while the regular PMs were kept at 30°C.

Road asphalt is composed from mineral matter that is mixed together with bitumen, a crude oil-based binding agent **(Wess et al., 2004)**. The bitumen of the asphalt that is currently used at Elgeseter street was provided by the Norwegian Public Roads Administration. Two triplets of new tire samples that included a summer, studded (winter), and non-studded (winter) tire were obtained for both light- (passenger) and heavy-(trucks) duty vehicles. In addition, a background soil sample was collected from a forest location on the outskirts of the city, with the aim to establish background concentrations in the Trondheim area. Approximately 2 g from the soil sample was dewatered by freeze-drying, thereafter ground into a fine powder using a mortar and pestle and stored at −20 °C until analysis.

Overall, 32 (2 campaigns x 16 samples) WDS-, 4 Prall-, 8 APM, 6 tire, 1 bitumen, and 1 soil sample(s) were analyzed for BTRs and BTHs; 52 samples in total. For elemental analysis, 20 (2 campaigns x 10 samples) WDS-, 2 Prall-, 8 APM, and 1 soil sample(s) were analyzed; 31 samples in total.

### 2.3. Sample Preparation for Organic Analytes in Dissolved Phase and PM

Extraction and isolation of target analytes from the environmental samples were performed by Strata™-X cartridges according to **Asimakopoulos et al. (2013b)** with minor modifications (see *Supplementary data* for details).

### 2.4. Sample Preparation for Organic Analytes in Tires and Bitumen

A portion of 100 mg (±10 mg) of bitumen or tire sample was transferred into a 15 mL Eppendorf$^{®}$ tube. The tire sample portions were removed with clean scissors and tweezers from the rubber surfaces of the tires and were dissolved with 1 mL DCM. Thereafter, 5 mL of acidified Milli-Q water/MeOH solution (1:1 % v/v, adjusted with HCl solution to pH<3) were added. The bitumen sample was dissolved with 5mL DCM, and 100 µL of bitumen solution was transferred into a new Eppendorf® tube and 5 mL of acidified Milli-Q water/MeOH solution (1:1 % v/v, adjusted with HCl solution to pH <3) were added. Thereafter, sonication was performed for both matrices for 45 min, followed by centrifugation for 10 min. A volume of 1 mL of the supernatants was transferred for liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis.

### 2.5. Sample Preparation for Elemental Analysis in Dissolved Phase

A portion of 10 mL of WDS- or Prall-sample was filtered into a 15 mL Eppendorf® tube using a syringe and a syringe filter. The filtered sample was acidified with purified concentrated nitric acid (pH<2) for conservation purposes and transferred for high-resolution inductively-coupled plasma mass spectrometry (HR-ICP-MS) analysis. The 2.5 mL extract that was obtained from each APM filter **(see 2.4.)** was diluted to 16.5 mL with Milli-Q water and acidified with nitric acid (0.1 M).

### 2.6. Sample Preparation for Elemental Analysis in Turbid Phase

A portion of 9 mL of unfiltered WDS- or Prall-sample was transferred to a polytetrafluoroethylene (PTFE) vessel, and 2 mL pure concentrated nitric acid was added. A portion of 230 mg (±10 mg) of soil sample was transferred to a PTFE vessel, and 9 mL of aqueous nitric acid (50% v/v) were added. Digestion of the samples was carried out in a high-pressure microwave system according to a step-temperature program. After the digested samples cooled down to room temperature, they were diluted with Milli-Q water and transferred for HR-ICP-MS analysis.

### 2.7. LC-MS/MS Analysis

Instrumental analysis of BTRs and BTHs were performed according to **Asimakopoulos et al. (2013 a,b,c)** with minor modifications. In the present study, two additional BTR derivatives were added to the list of target chemicals (BTR-COOH and 5-ABTR). The chromatographic separation was carried out using an *Acquity UHPLC Thermo system (Waters, Milford, U.S.)*. The tandem mass spectrometric system was a *Xevo TQ-S, triple quadrupole mass analyser (QqQ)*, with a *ZSpray ESI* function (*Waters, Milford, USA)*. The LC column used was an Atlantis C18 T3 (150 mm × 2.1 mm, 3 $\mu$m) connected to a Phenomenex C18 guard column (4.0 mm × 2.0 mm, 5 $\mu$m). The instrumental lower limits of quantification (LLOQs), and the limits of detection (LOD) of the target analytes are presented in **Table S1**. Quantification of the target analytes was accomplished based on the internal standard method and with matrix-matched standard addition calibration standards prepared by spiking target analytes into the specified matrices prior to extraction **(Asimakopoulos et al., 2013b)**. More details concerning the LC-MS/MS analysis are available in *Supplementary data* **(Tables S2-S4)**.

## 2.8. HR-ICP-MS Analysis

Elemental analyses were performed using an *Element 2* instrument *(Thermo Finnigan model; Bremen, Germany)*. The samples were introduced using a combination of SC2 DX autosampler (with ULPA filter dust cover) and PrepFAST flow injection analysis system *(Elemental Scientific, Inc. Omaha, NE)* with a total flow of 200 $\mu$L/min. The instrument was equipped with a PFA-ST nebulizer, spray chamber (PFA Barrel 35 mm), demountable torch, quarts standard injector, sample cone and skimmer cones. Methane ($CH_4$) was introduced into Argon (Ar) gas to avoid the formation of oxides and provide enhanced sensitivity, especially for Se and As. The cool, auxiliary, nebulizer and T-connection gas flow was set at 15.5, 1.10, 0.75, and 0.55 L/min, respectively. The

LOQ of every element was set at the concentration where repeatability (RSD%) was 25 % **(Table S5)**.

### 2.9. Quality Assurance and Quality Control (QA/QC)

For the analysis, the contamination that arose from laboratory materials and solvents was evaluated by the analysis of procedural blanks; and was found for all chemicals <LOD. For each batch of 25 samples analyzed for organics, one procedural blank was analyzed simultaneously, and a calibration check standard was injected after every 20 samples as a check for drift in instrumental sensitivity. In addition, a methanol blank was injected after every two samples as a check for carry-over of target analytes between samples. For the elemental analysis, accuracy and reproducibility of the ICP-MS instrument was ensured by measuring 9 replicates of certified calibration solutions (see *Supplementary data* for details), and the frequent analysis of the customized reference soil material GBW 07408 (GSS-8) (Chinese National Center for Standard Materials). Instrumental repeatability of measurements was established for every individual sample by scanning it three consecutive times.

### 2.10. Data Analysis

LC-MS/MS data were acquired with the *IntelliStart*, *MassLynx* and *TargetLynx* software packages *(Waters, Milford, U.S.)*. HR-ICP-MS data treatment was performed with the built-in software of the *Element 2* instrument *(Thermo Finnigan model; Bremen, Germany)*. Excel *(Microsoft, 2010)* and SPSS Statistics *(IBM, version 25)* were used for general descriptive statistics and Pearson correlation analysis. Principal component analysis (PCA) was performed by the statistical software *R* (*https://www.R-project.org; 2018)*. Data analysis did not include censored data (i.e., nondetects;

NDs). The statistical significance was set at $p < 0.01$ (unless stated $< 0.05$). Log-transformed concentration values were used for the correlation analysis and PCA. Prior to the analysis, data columns with missing values were excluded while the data were centered and scaled.

## 3. Results and discussion

### 3.1. Profile of BTRs and BTHs in WDS-samples

All target organic chemicals were determined in the WDS-samples. The concentrations in PM (ng/g dry weight (d.w.)) and the dissolved phase (ng/L) are given in **Tables S6** and **S7**, respectively. The total concentrations (sum of PM and dissolved phase) are given in **Table 1** and were found to be ~2 and ~3 fold higher in the studded than the non-studded season for BTRs and BTHs, respectively. These differences correspond well to the ~3.5- fold higher particle amounts in the WDS-samples in the studded season. However, the concentration profile differences between seasons can be partially attributed to the different underlying environmental and weather conditions between seasons (e.g., colder temperatures and significantly decreased sunlight during the studded season). Different environmental conditions denote by-default differences in photochemical transformation processes, hydrolyses, and microbial degradation pathways **(AMAP, 2017)**. The median concentrations of the derivatives increased significantly in the studded season, except for 5-ABTR and 2-S-BTH that demonstrated a decrease; for 2-S-BTH the decrease was slight. In the non-studded season, 2-ABTH and 5-ABTR accounted for 13 and 42 % of the $\Sigma(6)$BTHs and $\Sigma(7)$BTRs, respectively, while in the studded season their percentage decreased to 5 and 8 %, respectively. It is documented that 2-ABTH is rapidly degraded in the presence of Cl **(Nika et al., 2017)**, suggesting a similar degradation pathway for 5-ABTR. 2-OH-BTH and TTR were the predominant chemicals in both seasons. The total median concentrations of BTR and TTR were 38.0 and 277 ng/L in the non-studded season, and 80.1 and 759 ng/L in the studded season, respectively. BTR was used in the past as a corrosion inhibitor (for Cu) in windshield fluid, patented by **Shell Oil Co (1976)**, but there are reports that it is currently also in use **(Trico Products, 2016)**. Thus, it is unknown whether both BTR and TTR are used in anti-icing/de-icing formulations for roads or/and windshield fluids (for vehicles) in Norway, but the strong correlation of those during the studded season ($r=0.99$, $p<0.01$; **Table S8**) suggests common pollution sources or/and applications.

**(Insert Table 1)**

### 3.2. Occurrence of BTRs and BTHs in Prall-samples, Bitumen and Soil

All target organic chemicals except BTH and XTR were determined in Prall-samples **(Table S9)**. The concentrations in PM (ng/g d.w.) and the dissolved phase (ng/L) are given in **Tables S10** and **S11**, respectively. The three significantly most abundant chemicals in Prall-samples are (in decreasing order): 2-OH-BTH > 2-Me-S-BTH > TTR. In bitumen, only 2-S-BTH was determined (1.86 ng/g d.w.), while in soil, only three chemicals were detected, namely, 2-S-BTH (3.55 ng/g d.w.), 2-Me-S-BTH (1.78 ng/g d.w.), and 5-ABTR (28.2 ng/g d.w.). Therefore, the contribution of soil and bitumen to the organic chemical content of Prall-samples was insignificant. The detected BTHs and BTRs in Prall-samples potentially derive from either direct addition, impurities in other asphalt additives such as mineral adhesives (amines and amides) and recycled tire granules **(Markiewicz et al., 2017; Llompart et al., 2013)** or contamination during asphalt manufacturing and installation. To our knowledge, only mineral adhesives have been added in the asphalt used at Elgeseter street.

## 3.3. Distribution coefficient values ($K_d$; in L $kg^{-1}$) for BTRs and BTHs in WDS- and Prall-samples

$K_d$ values were calculated as the ratio of the concentration of each compound in particulate phase (ng/kg), to the concentration of target compound in dissolved phase (ng/L). $K_d$ values are given in **Table 2** for those chemicals with detectable concentrations in dissolved and particulate phases. These values show a trend in distribution, even though they demonstrate high uncertainties, as they represent median values. Both BTRs and BTHs, except from 2-Me-S-BTH, presented significantly higher affinity for particulates in the WDS-samples of the studded- than the non-studded season. In the non-studded season, 2-S-BTH demonstrated an ~3-fold increase in affinity for particulates, while 2-Me-S-BTH demonstrated a decrease of the same level of magnitude. Furthermore, 2-S-BTH, 2-Me-S-BTH, 2-ABTH and TTR presented higher affinity to the particulates of Prall- than WDS-samples. In addition, BTRs and BTHs demonstrated higher affinity to the road and asphalt dust than wastewater sludge, as shown by comparing our $K_d$ values with previous work on wastewater sludge **(Stasinakis et al., 2013)**.

**(Insert Table 2)**

## 3.4. BTRs and BTHs content in Tires

All target BTHs, XTR and 1-OH-BTR were determined in tires **(Table S12)**. The rank order of Σ(6)BTHs (average) concentrations in tires was (in decreasing order): non-studded (37 644) > summer (16675) > studded (10265 ng/g). Interestingly, the BTH content was ~4-fold higher in the non-studded than the studded winter tires. BTH and 2-S-BTH concentrations were found higher in all tires for light-duty vehicles, while 2-OH-BTH was found higher in all tires for heavy-duty vehicles. 2-S-BTH was the derivative with the higher abundance in tires, followed by BTH and 2-OH-BTH; the predominance of 2-S-BTH agrees with previous literature **(Herrero et al., 2014)**. 2-Me-S-BTH concentration was found 2-fold higher in the non-studded tires of heavy- than light- duty vehicles. 2-M-BTH was detected only in the summer and studded tires for heavy-duty vehicles. 1-OH-BTR was detected in half of the samples, while XTR was detected in traces (<1 ng/g) in summer and studded tires for light-duty vehicles. Our results confirm that the composition of the tires found in vehicles is highly dependent on the type of the vehicle for which they are designed to be used **(Markiewicz et al., 2017)**.

### 3.5. Profile of BTRs and BTHs in APM samples

All BTHs, except 2-M-BTH, BTR and TTR were detected in the APM samples **(Table S13)**. The highest amounts were found for 2-OH-BTH (302) and BTR (4065 pg) in the $PM_{2.5-10}$ and volatile $PM_{2.5}$ filters, respectively. The results indicate the presence of BTRs and BTHs in $PM_{2.5}$ and $PM_{2.5-10}$. The rank order of Σ(7)BTRs amounts in APM samples was (in decreasing order): Volatile $PM_{2.5}$ (4065) > Volatile $PM_{2.5-10}$ (1125) > $PM_{2.5-10}$ (50.1 pg) > $PM_{2.5}$ (not detected). The rank order of Σ(6)BTHs (average) amounts in APM samples was (in decreasing order): $PM_{2.5-10}$ (200) > Volatile $PM_{2.5}$ (188) > $PM_{2.5}$ (91.5) > Volatile $PM_{2.5-10}$ (36.1 pg). The findings indicate higher volatility for BTRs than BTHs; consequently, BTHs are more prone to re-suspend/bind to road dust than BTRs.

### 3.6. Trace Elements in soil, WDS-, Prall-, and APM sample(s)

The minerals in the coarse aggregate at Elgeseter street mainly consist of plagioclase ($Na(AlSi_3O_8)$ and $Ca(Al_2Si_2O_8)$), quartz ($SiO_2$) and amphibole (Mg-Fe silicate) **(Erichsen et al., 2004)**. The elements that were found in higher concentrations in the soil **(Table S14)**, WDS-, and Prall-samples **(Table S15)** were: Si, Al, Ca, Na, Fe and Mg; supporting the statement of **Pant and Harrison (2013)**, that the crustal dust is a main contributor to road dust. The concentrations of the crustal elements were significantly higher in the studded season, supporting that the winter-sanding of the road, and the use of studded tires increases substantially the road surface weathering **(Schauer et al., 2006)**. The concentrations of all elements in filtered WDS- and Prall-samples, which contain only fine particles (< 0.45 μm), were significantly lower as previously reported in the literature **(Table S16) (Schauer et al., 2006)**. In line with this, the coarse APM samples demonstrated higher concentrations than the fine APM samples **(Table S17)**. Most elements demonstrated higher concentrations in the volatile $PM_{2.5}$ and volatile $PM_{2.5-10}$ filters, indicating considerable element volatility. As, Cu, Pb, S, Sn, Ni, P, W and Ti demonstrated equal or higher concentrations in both the $PM_{2.5}$ and $PM_{2.5-10}$ filters compared to their respective volatile filters, indicating a higher tendency to re-suspend/bind to road dust. The concentration of Cl in WDS-samples was ~80-fold higher in the studded season due to the salt addition on the road surface during winter. This Cl concentration was correlated with Na ($r=0.79$; $p< 0.05$), Mg ($r=0.92$; $p< 0.01$), and Ca ($r=0.78$; $p< 0.01$) concentration in the studded season since NaCl is added to prevent/remove ice, while $CaCl_2$ and $MgCl_2$ are used as de-icing and dust binding chemicals at Elgeseter street. The concentration of Sb, which is a major component in brake dust **(Fukuzaki et al., 1986; Schauer et al., 2006)**, was similar in the non-studded (median: 10.6 ng/mL) and studded (median: 11.3 ng/mL) season, indicating similar pollution sources independent of season. Ni and V have previously been reported in exhaust emissions due to engine oil combustion and were found ~ 4-5-fold higher in the studded season **(Pant and Harrison, 2013)**. In addition, the elements that are present in gasoline and diesel gas, including, Br, Zn, V, Cd, Pb, Ba, Cu, Mn and

Sr **(Cheng et al., 2010; Lin et al., 2005)**, demonstrated higher concentrations in the studded season. These increased concentrations in the studded season are attributed to the increased fuel consumption during winter due to colder temperatures. Numerous correlations were identified herein between the total concentrations of trace elements, BTRs and BTHs in all WDS-samples (independent of season) **(Table S18)**; these correlations were attributed to BTRs and BTHs forming complexes with elements, particularly metals **(Fateh et al., 2017)**.

### 3.7. BTR and TTR as markers of metal corrosion

Al, Cu, Fe, and Zn demonstrated strong positive correlations with Cl in the WDS-samples in the studded season: Al ($r=0.93$; $p< 0.01$); Cu ($r=0.95$; $p< 0.01$); Fe ($r=0.91$; $p< 0.01$); and Zn ($r=0.97$; $p< 0.01$). The 4 metals, namely, Al, Cu, Fe, and Zn are reported in abundance in the brake linings, chassis, wheels, and shocks of vehicles **(Cole, 2017; Thorpe and Harrison, 2008)** and it is documented that road salt contributes to their corrosion **(Kogel et al., 2006)**. Al, Cu, Fe, and Zn demonstrated also strong positive correlations with BTR and TTR in both the non-studded and studded seasons ($r=0.84$-$0.99$, $p<0.01$), while BTR and TTR demonstrated strong positive correlations with Cl ($r>0.96$, $p< 0.01$) only in the studded season. These findings indicate that BTR and TTR are valuable markers of metal corrosion that derive from vehicles.

### 3.8. Principal Component Analysis: “Fingerprinting” the sample matrices

PCA was applied to identify the patterns and associations within specific data sets. The points that are proximal in the loading plots denote similar variability in their data. On the basis of the data sets that were analyzed herein, 4 different PCAs were performed, and the scores and loadings plot for each PCA are presented combined in a biplot. Each variable can be depicted with an arrow, and the longer the length of the arrow, the greater the contribution of the variable to a given component.

*Data Set I-Total concentrations of Σ(7)BTRs and Σ(6)BTHs in Tires, WDS-, APM, and Prall-samples.* For the creation of this data set we used pairwise sums of BTRs and BTHs concentrations, and it was possible to group together the samples from different matrices **(Figure S1)**. However, only the tires were clearly separated from the other matrices on the basis of BTRs and BTHs content. The loadings demonstrate differences in the applications or/and pollution sources of BTRs and BTHs even though they are both anticorrosive/antifreeze agents with similar structures.

*Data Set II-Total concentrations of Trace Elements in WDS-, APM, and Prall-samples.* In this data set, not only there was a clear separation of road dust between the studded and non-studded season, but also between the road dust and APM samples **(Figure S2)**. However, the Prall-samples that were collected in the non-studded season were grouped together with the WDS-samples of the same season. This finding supports that elements from road dust, or other sources, can be incorporated into the asphalt (road surface), as previously stated by **Thorpe and Harrison (2008)**. From the PCA loadings it was demonstrated that due to the complexity of interactions between sources of elemental input in the urban road setting, it is not possible to pinpoint with certainty specific markers of traffic pollution by assessing only the elements. However, one or more element(s) formed 6 distinct groups that denote positive (co)variance (within each group): (1) B, Cl, Au; (2) Zn; (3) Cd; (4) S; (5) Ag, Ba, Br, Na, Cu, K, Ti, As, Bi; and (6) Ta. In group (1), B and Cl are highly volatile elements, while Au is moderately volatile, and these variables contribute positively to the APM samples **(Benz et al., 1999)**. In group (2), Zn was previously proposed as a tracer for tire wear, but it is not reliable when used solely, since it is emitted by several other sources (crustal and anthropogenic) **(Thorpe and Harrison, 2008)**. The elements Zn, S, Ba, Na, Cu, K, Ti, and As (from groups 3, 4 and 5) derive from car brake dust (among other documented sources), and according to the biplot, these variables contribute positively to the WDS-samples in the studded season denoting higher metal wearing. The strong positive covariance of Zn and S in the WDS-samples in the studded season denotes the presence of rubber particles in road dust **(Schauer et al., 2006)**. The major source of Bi is from impurities of refining Pb, Cu, Sn, Ag and Au ores (http://www.rsc.org/periodic-table/element/83/bismuth). In group (6), Ta is solely separated from the other elements due to its uniquely high corrosion-resistance **(Hampel, 1961)**. Thus far, numerous research studies have concluded to use simple diagnostic ratios to pinpoint specific pollution sources of road traffic. For instance, the Cu:Sb concentration ratio is commonly applied in an attempt to pinpoint metal surface wear from vehicles (e.g., brake wear) **(Thorpe and Harrison, 2008)**. Nonetheless, in the biplot, the loadings of Cu and Sb did not present the strongest contributions, meanwhile they were found correlated with numerous other elements that provide similar contributions (e.g. Ti, Sr, Li) **(Figure S2)**.

*Data Set III-Total concentrations of BTRs, BTHs and Trace Elements in WDS- and Prall- samples.* By combining the inorganic and organic target chemicals in this dataset, new markers of traffic pollution were identified based on positive covariances. In this data set, pairwise sums of BTRs and BTHs concentrations were also used, and there was a clear separation in the score-plot between the road dust and the Prall-samples **(Figure 1)**.

**(Insert Figure 1)**

As in data set II, one or more target chemicals(s) formed 6 distinct groups: (1) 2-S-BTH, 2-ABTH, Σ(7)BTRs, Sb; (2) Sn, TTR, Bi, Pb; (3) BTR, 5-Cl-BTR, Mo; (4) Th, Br, Cr, Nb, Ba, Sr, K, Σ(6)BTHs, 2-OH-BTH, Cl, Na; (5) 2-Me-S-BTH, 2-OH-BTH, Cl, Na; and (6) Ta. In group (1), 2-S-BTH was strongly associated to Sb, since Sb is derived from brake wear **(Thorpe and Harrison, 2008)**, while 2-S-BTH is the most abundant chemical found in tires **(Table S12)**. In group (5), 2-Me-S-BTH, the methylation product of 2-S-BTH, was strongly associated with Cl (and Na) which is in abundance in the studded season. The conversion of 2-S-BTH to 2-Me-S-BTH is promoted aerobically through bacteria in soil, sediments, and water isolates **(De Wever and Verachtert, 1997)**, but also favored in the presence of alkyl (and acid) halides under specific oxidizing environmental conditions. **Narkhede et al. (2007)** reported that under laboratory conditions, energy-assisted alkylation was favored when 2-S-BTH reacted with alkyl halides on a setting where $SiO_2$ and $Al_2O_3$ are in abundance **(eq. S1)**. Thus, due to the highly reactive nature of the free thiol group of 2-S-BTH, and the high abundance of the methyl radicals ($CH_3\cdot$) in the environment, it can be hypothesized that 2-S-BTH partially converts to 2-Me-S-BTH (among other products) once leached from the tires into the environment. This statement is supported by the occurrence data, where 2-S-BTH and 2-Me-S-BTH concentrations were found (on average) in tires between 5038-13807 and 111-197 ng/g, respectively **(Table S12)**, and in WDS-samples between 9.25-12.6 and 41.2-126 ng/L, respectively **(Table 1)**; the concentrations of 2-Me-S-BTH were higher in the road dust, but significant lower than 2-S-BTH concentrations in tires. Consequently, 2-Me-S-BTH functions as a marker of tire chemical leaching, while 2-S-BTH serves as a marker for particle emissions (physical tear/wear) from the tires. 2-ABTH was the derivative that demonstrated the highest positive covariance to 2-S-BTH **(Figure 1)**. In addition, in group (5) a co-variance of 2-

OH-BTH with Cl (and Na) was identified, denoting possible chemical leaching of hydrolyzed BTH from tires. The presence of 2-OH-BTH indicates an aerobic degradation pathway of BTH **(Felis et al., 2016)**. In groups (2) and (3), there is an association of BTRs with Sn, Bi, Pb, and Mo that denotes a likelihood for metal abrasion, while in group (4) the association of Σ(6)BTHs and 2-OH-BTH to the elements of this group could not be directly linked to either tire or/and metal abrasion.

<u>Data Set IV-</u> *Concentrations of BTRs, BTHs and Trace Elements in the dissolved phase of WDS- and Prall- samples.* Compared to the previous data set that was based on the total concentrations, this data set was based on the dissolved phase concentrations found in WDS- and Prall-samples. Again, pairwise sums of BTRs and BTHs concentrations were used. The fine particulate matter (<2 μm) concentrations of WDS- and Prall-samples that were represented by the dissolved phase concentrations, provided a clear separation of seasons on the score plots between the studded and non-studded WDS-samples **(Figure S3)**. To gain a better understanding of the loadings, we have divided the variables into 18 distinct groups: (1) Fe; (2) Ti; (3) Ce, La, Nd, Y, Tb, Dy, Gd, Sc; (4) Pr; (5) Cu, Pb, Zr, Th, Cr, Ho; (6) Ni, Bi; (7) P, Zn; (8) Cd; (9) V; 10) Eu, Sr; 11) Ca, Si, Al, U, S; (12) Na, Ga, Tl, Σ(6)BTHs, K, Cl, Br, Co, Mn; (13) Rb, Mg, Cs; (14) Li; (15) B; (16) W; (17) As, Mo; and (18) Sn, Ba, Sb, Σ(7)BTRs. Groups (1) to (4) demonstrated a strong contribution to the Prall-samples, which indicates crustal element inputs. Group (6) contributed equivalently to the Prall- and WDS-samples (in the non-studded season) denoting that Ni and Bi are possibly attributed from both crustal abundance and traffic emissions. V contributed negatively to the Prall-samples, attributing this element to anthropogenic activities rather than crustal origin. Si, Ca, Na, Mg, Al, S and Sr that are included in groups (10-13) are dust re-suspension markers **[5]** and demonstrate a positive contribution alongside with Li, B and W, to the WDS-samples in the

studded-season. Σ(6)BTHs are associated with the elemental dust re-suspension markers indicating tire wear particles re-suspension. In group (17), the weak contribution of As with the strong contribution of Mo indicates car brake lining wear **(Thorpe and Harrison, 2008)**. Σ(7)BTRs were positively associated with Sn, Sb, and Ba loadings that are mainly linked to brake wear.

### 3.9. Human Exposure Assessment to BTRs and BTHs through inhalation

The estimated daily intake (EDI; pg/kg-bw per day) of BTRs and BTH through road dust was calculated based on the concentrations found in the APM samples. The exposure estimation for BTRs and BTHs was performed on the basis of **equation S2**; a simplified version of the equation used previously for BTHs by **Zhang et al. (2018)**.

**(Insert Table 3)**

Children are assumed to weigh 15 kg and adults 70 kg, while the inhalation rate was set to 7.6 and 20 $m^3$/day for children and adults, respectively **(Zhang et al., 2018)**. The BTHs concentrations reported here were significantly lower (pg range) than those reported in an urban road setting in China, where they were found in the ng range **(Zhang et al., 2018)**. The use of APM samples for EDI through inhalation was considered a realistic exposure scenario. However, the pharmacokinetics of BTRs and BTHs are thus far not well known; we assumed that BTRs and BTHs are totally inhaled by humans. Our findings suggest that BTRs demonstrate higher EDIs than BTHs; and BTRs concentrations are significantly higher in $PM_{2.5}$ than $PM_{2.5-10}$ (volatile), which indicates a higher human risk.

## 4. Conclusions

In summary, all target BTHs and BTRs were determined in the WDS-samples, thus indicating ubiquitous occurrence of these chemicals in road dust. This is the first study to report BTR and TTR, as suitable markers of metal corrosion, while 2-thio-benzothiazole and 2-methylthio-benzothiazole, as suitable markers of tire rubber particles and tire chemical leaching, respectively. Our findings suggest the need for further field studies to assess the effects on chemical markers of traffic pollution in an urban road setting during different weather conditions. Exposures of BTRs and BTHs must be further studied in humans in order to provide an insight into the pharmacokinetics of BTRs and BTHs. The association of concentrations with underlying environmental conditions between seasons was tempered in this study by the small sample size, and, therefore, no further conclusions were drawn in this regard. The results of this study provide baseline information on exposures to select environmental pollutants from a heavily trafficked sub-Arctic road setting.

## Supplementary data

Details showing standards, materials and laboratory procedures. Tables showing the parameters for the analysis, the analytical method performance characteristics, Pearson correlations among target chemicals, and concentrations of target chemicals found in different dissolved phase and PM matrices. Figures showing the PCA biplots. Equations showing the transformation conditions of 2-S-BTH to 2-Me-S-BTH and the calculation of the EDI values.

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## Notes

The authors declare no competing financial interest.

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**Table 1.** Total Concentrations (ng/L; sum of the dissolved phase and PM) of BTHs and BTRs in WDS-samples.

| | WDS-samples from the Non-Studded Season | | | | | WDS-samples from the Studded Season | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Analytes | Median (ng/L) | Average (ng/L) | Min (ng/L) | Max (ng/L) | Detection rate | Median (ng/L) | Average (ng/L) | Min (ng/L) | Max (ng/L) | Detection rate |
| BTH | 30.7 | 35.5 | 9.74 | 66.4 | 10/16 | 127 | 127 | 40.5 | 203 | 9/16 |
| 2-S-BTH | 12.7 | 12.6 | 6.79 | 19.0 | 16/16 | 8.83 | 9.25 | 1.72 | 19.4 | 16/16 |
| 2-OH-BTH | 197 | 232 | 26.6 | 522 | 16/16 | 692 | 729 | 245 | 1404 | 16/16 |
| 2-ABTH | 42.4 | 52.0 | 27.0 | 162 | 16/16 | 52.8 | 59.1 | 26.9 | 134 | 16/16 |
| 2-Me-S-BTH | 35.3 | 41.2 | 16.8 | 116 | 16/16 | 125 | 126 | 77.4 | 195 | 16/16 |
| 2-M-BTH | 1.33 | 1.92 | 0.06 | 9.21 | 16/16 | 3.54 | 3.47 | 1.72 | 6.61 | 16/16 |
| Σ(6)BTHs | 303 | 361 | 93.4 | 801 | 16/16 | 939 | 1006 | 360 | 1903 | 16/16 |
| BTR | 38.0 | 41.7 | 20.8 | 70.8 | 16/16 | 80.1 | 82.1 | 43.4 | 135 | 16/16 |
| TTR | 277 | 335 | 157 | 1239 | 16/16 | 759 | 761 | 386 | 1260 | 16/16 |
| XTR | 4.14 | 4.12 | 4.14 | 4.12 | 1/16 | 1.88 | 14.1 | 1.21 | 86.3 | 7/16 |
| BTR-COOH | 23.4 | 27.8 | 8.95 | 52.9 | 16/16 | 10.4 | 14.1 | 4.14 | 29.2 | 16/16 |
| 5-Cl-BTR | 4.36 | 7.17 | 1.11 | 37.9 | 16/16 | 7.19 | 8.51 | 3.43 | 19.8 | 16/16 |
| 1-OH-BTR | 4.43 | 6.68 | 0.77 | 22.2 | 10/16 | 51.1 | 67.3 | 14.5 | 213 | 16/16 |
| 5-ABTR | 256 | 266 | 92.5 | 471 | 9/16 | 78.8 | 536 | 40.2 | 2251 | 5/16 |
| Σ(7)BTRs | 529 | 557 | 191 | 1308 | 16/16 | 977 | 1106 | 473 | 3054 | 16/16 |

**Table 2.** Distribution coefficient values, $K_d$ (average; L $kg^{-1}$) for BTRs and BTHs in WDS- and Prall-samples

| | WDS-samples from the non-studded season | | WDS-samples from the studded season | | Prall-samples | |
|---|---|---|---|---|---|---|
| Analytes | $K_d$ (L/Kg) | ±SD[*] | $K_d$ (L/Kg) | ±SD | $K_d$ (L/Kg) | ±SD |
| BTH | n.c.[#] | n.c. | 93.9 | n.c. | n.c. | n.c. |
| 2-S-BTH | 1953 | 1178 | 635 | 753 | 4114 | 2689 |
| 2-OH-BTH | 23724 | 23231 | 450 | 4782 | 1077 | 1789 |
| 2-ABTH | 642 | 286 | 174 | 80.1 | 931 | 409 |
| 2-Me-S-BTH | 1355 | 2449 | 3005 | 3078 | 30122 | 24055 |
| 2-M-BTH | n.c. | n.c. | 567 | 398 | 528 | 178 |
| BTR | 2608 | 895 | 368 | 174 | 929 | n.c. |
| TTR | 1682 | 610 | 295 | 118 | 4383 | 2183 |
| XTR | n.c. | n.c. | 523 | 442 | n.c. | n.c. |
| BTR-COOH | 5033 | 3653 | 417 | 253 | n.c. | n.c. |
| 5-Cl-BTR | 2728 | 7598 | 2219 | n.c. | n.c. | n.c. |
| 1-OH-BTR | n.c. | n.c. | 524 | 366 | n.c. | n.c. |
| 5-ABTR | n.c. | n.c. | n.c. | n.c. | n.c. | n.c. |

*SD: Standard Deviation; [#]Not calculated.

**Table 3.** Estimated Daily Intake (pg/kg-bw/day) of BTHs and BTRs

| APMs | $PM_{2.5}$ | | Volatile $PM_{2.5}$ | | $PM_{2.5\text{-}10}$ | | Volatile $PM_{2.5\text{-}10}$ | |
|---|---|---|---|---|---|---|---|---|
| Group population | Children | Adults | Children | Adults | Children | Adults | Children | Adults |
| Σ(6)BTHs | 0.16 | 0.09 | 0.33 | 0.19 | 0.35 | 0.20 | 0.06 | 0.04 |
| Σ(7)BTRs | - | - | 7.15 | 4.03 | 0.09 | 0.05 | 1.98 | 1.12 |

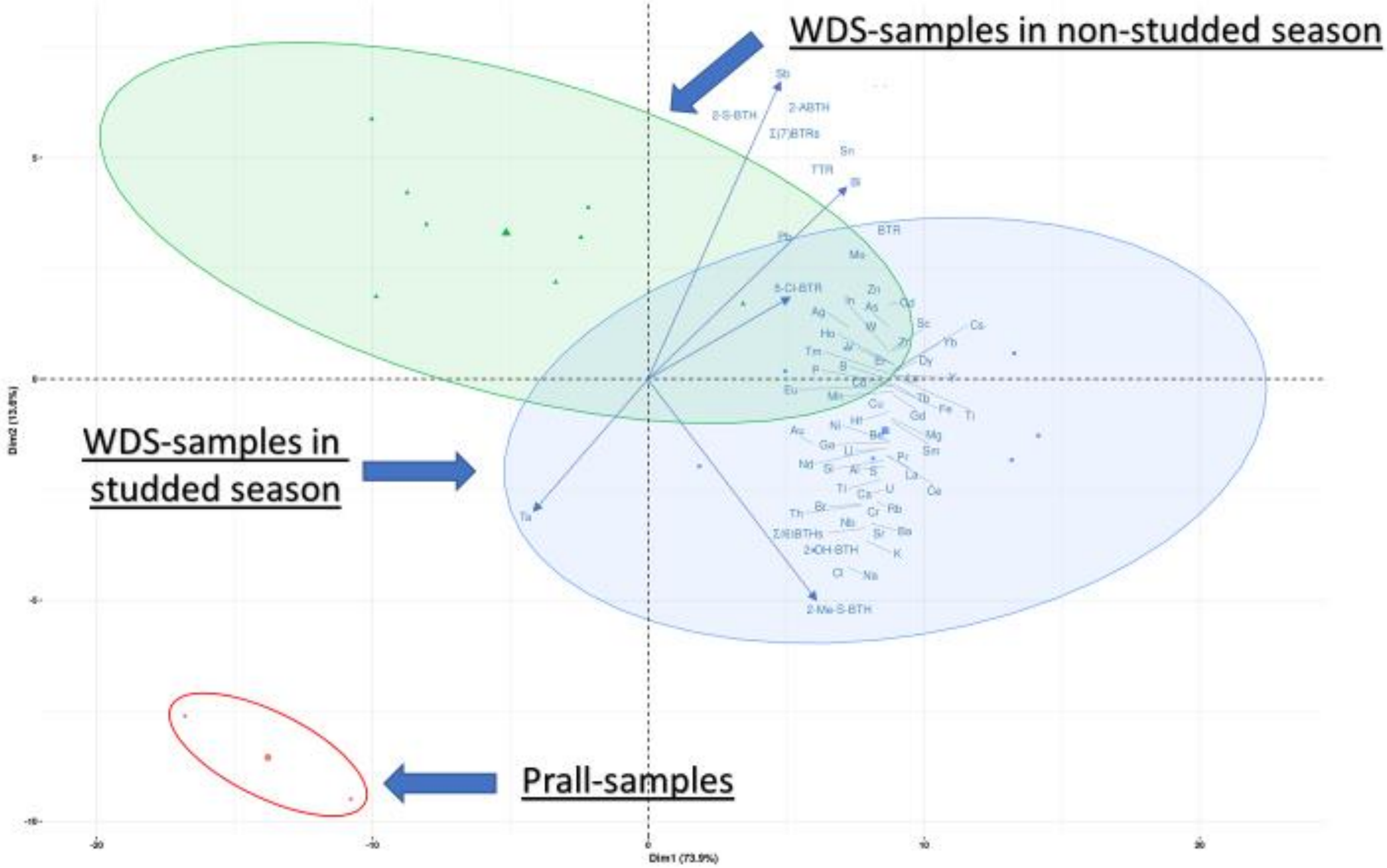

**Figure 1.** Principal component analysis biplot of classification of matrices based on the concentrations of BTRs, BTHs, and trace elements.