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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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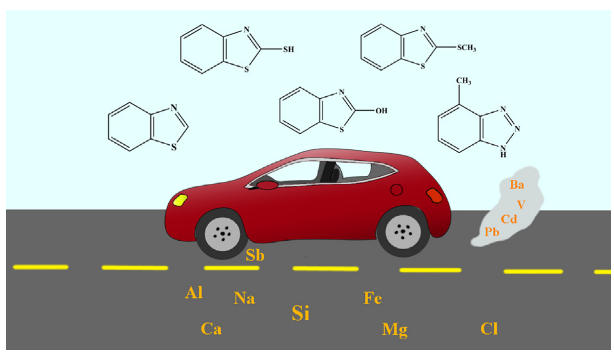
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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

Abbreviations: BTHs, benzothiazoles; 2 S BTH, 2 mercaptobenzothiazole; BTH, benzothiazole; 2 OH BTH, 2 hydroxy benzothiazole; 2 M BTH, 2 morpholin 4 yl benzothiazole; 2 Me S BTH, 2 methylthio benzothiazole; 2 ABTH, 2 aminobenzothiazole; BTRs, benzotriazoles; BTR, 1H benzotriazole; TTR, tolyltriazole; 1 OH BTR, 1 hydroxy benzotriazole; BTR COOH, benzotriazole 5 carboxyl acid; 5 Cl BTR, 5 chloro 1H benzotriazole; XTR, xylyltriazole; 5 ABTR, 5 amino 1H benzotriazole; LLOQ, Lower Limit of Quantification; LOD, Limit of Detection; R.S.D., Relative Standard Deviation; WDS, Wet Dust Sampler; PM, particulate matter; (QA/QC), quality assurance/quality control; HDPE, high density polyethylene; APM, airborne particulate matter.

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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.

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, 1968; 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*, *U.K.*). 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.