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journal homepage: www.elsevier.com/locate/envpolTraffic-related distribution of antimony in roadside soils[☆]Corinna Földi^{a,*}, Simon Saueremann^a, Reiner Dohrmann^b, Tim Mansfeldt^a^a Department of Geosciences, Soil Geography/Soil Science, University of Cologne, D-50923 Köln, Germany^b Bundesanstalt für Geowissenschaften und Rohstoffe (BGR)/Landesamt für Bergbau, Energie und Geologie (LBEG), Stilleweg 2, D-30655 Hannover, Germany

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ABSTRACT

Vehicular emissions have become one of the main source of pollution of urban soils; this highlights the need for more detailed research on various traffic-related emissions and related distribution patterns. Since the banning of asbestos in the European Union, its substitution with antimony (Sb) in brake linings has led to increased inputs of this toxic metalloid to environmental compartments. The objective of this study was to provide detailed information about the spatial distribution patterns of Sb and to assess its mobility and bioavailability. Roadside soils along an arterial road (approx. 9000 vehicles per day) in Cologne (Germany) were studied along five transects, at four soil depths and at seven sampling points set at varying distances from the road ($n = 140$). For all samples, comprehensive soil characterization was performed and inverse aqua regia-extractable trace metal content was determined being pseudo-total contents. Furthermore, for one transect, also total Sb and a chemical sequential extraction procedure was applied ($n = 28$). Pseudo-total Sb for all transects decreased significantly with soil depth and distance from the road, reflecting a distribution pattern similar to that of other trace metals associated with brake lining emissions. Conversely, metals associated with exhaust emissions showed a convex distribution. The geochemical fractionation of Sb revealed the following trends: i) non-specifically sorbed Sb was <5%; ii) specifically sorbed Sb was only detected within 1 m distance from the road and decreased with depth; iii) Sb associated with poorly-crystalline Fe oxides decreased with distance from the road; and iv) content of Sb bounded to well-crystalline Fe oxides, and Sb present in the residual fraction remained relatively constant at each depth. Consequently, roadside soils appear to inhibit brake lining-related Sb contamination, with significant but rather low ecotoxicological potential for input into surface and groundwater.

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1. Introduction

Demographic growth and progressive urbanization have contributed to a rapid increase in traffic density and highway infrastructure in urban areas, in turn leading to elevated vehicular emissions on a large scale. Several studies have identified road traffic emissions as a major source of diffuse trace metal pollution of urban soils. Since emissions from industry and other point sources have decreased significantly, diffuse contamination has become increasingly relevant in recent decades (Amato et al., 2011; Carrero et al., 2013; Hjortenkrans et al., 2007; Zhao and Hazelton, 2016). Given the above, there has been an increasing recent focus

on roadside soils for assessment of anthropogenic metal pollution, with several authors observing that roadside soils have high trace metal content originating from traffic-related emissions (Carrero et al., 2013; Chen et al., 2010; Wei and Yang, 2010). Most studies, however, focus only on well-known traffic-related pollutants, such as lead (Pb), cadmium (Cd), and zinc (Zn) (Bretzel and Calderisi, 2006; Nikolaeva et al., 2017; Viard et al., 2004); antimony (Sb) has only been addressed to a lesser extent.

Anthropogenic inputs of Sb are of environmental relevance, as international environmental protection agencies (Council of the European Communities, 1976; United States Environmental Protection Agency, 1979) consider Sb and its compounds to be a priority pollutant for which there is no known human requirement. Its toxicity largely depends upon its speciation; organo-antimonials are less toxic than pentavalent Sb (SbV, antimonate, and its species, e.g. $\text{Sb}(\text{OH})_3$), which in turn is less toxic than trivalent Sb (SbIII, antimonite, and its species, e.g. $\text{Sb}(\text{OH})_6^-$) (Filella et al., 2002; Gebel,

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1997). Antimonite is genotoxic and has carcinogenic potential (Gebel, 1997).

From the late 1980s onwards, the ban on use of asbestos in brake linings in the European Union and resulting replacement by Sb has led to increased inputs of the latter to environmental compartments. Antimony is added to friction material as a lubricant and comprises up to 5% of brake linings, mostly in the form of stibnite (Sb_2S_3) (Matejka et al., 2011; von Uexküll et al., 2005). According to the Zentrum für Umweltmessung und Umwelterhebungen und Gerätesicherheit Baden-Württemberg (UMEG) (2005), Sb_2S_3 is heated and hence vaporized during the braking process, producing a film on the surface of the brake. Differentiation via selective solubility shows that considerable amounts of Sb_2S_3 are oxidized during the braking process, most likely leading to the formation of antimony trioxide (Sb_2O_3), in turn classified as a possible human lung carcinogen (von Uexküll et al., 2005). Varrica et al. (2013) recently proved the existence of Sb_2O_3 in brake linings as well as in several particulate matter (PM) samples analyzed by X-ray absorption near edge structure (XANES). The authors further suggested that antimony mixed oxides (Sb_2O_4) were formed during brake abrasion. These Sb compounds most likely form a coating on PM released during the braking process and hence accumulate in urban environments. Hagino et al. (2016) recently summarized varying emission factors of Sb as function of vehicle type and road constructional settings; emissions on an inter-urban freeway with free-flowing traffic were 4–18 $\mu\text{g km}^{-1}$ per vehicle (light duty vehicles) and 44–128 $\mu\text{g km}^{-1}$ per vehicle (heavy duty vehicles), while emissions increased dramatically to 144 $\mu\text{g km}^{-1}$ per light duty vehicle in a street canyon in Stockholm (Sweden).

In addition to the potential dangers of direct exposure of humans to Sb via inhalable compounds, the deposition of brake lining-related Sb in roadside soils and its potential leaching into groundwater are also of ecotoxicological concern. Larger particles, either $\text{PM}_{2.5-10\mu\text{m}}$ or even $\text{PM}_{>10\mu\text{m}}$, are of special concern due to their more rapid deposition in soils or surface waters resulting from rapid gravitational settling; these could thus potentially be deposited right on the road surface or on roadside soils. Carrero et al. (2013) analyzed roadside soils in Spain for various trace, minor, and major elements, highlighting elevated content of Sb (mean: 1.5 mg kg^{-1}). For comparison purposes, background values of Sb in unpolluted soils are reported to range between 0.2 and 1.0 mg kg^{-1} depending on geological parent material (Amereih et al., 2005; Smith and Huyck, 1999; Utermann et al., 2008). Amereih et al. (2005) analyzed the distribution of Sb and its inorganic species in roadside surface soils (0–5 and 5–10 cm) along two highly trafficked routes in Austria. The authors confirmed significant accumulation of Sb on the soil surface, with levels exceeding natural background values more than ten-fold and four-fold along the two routes, respectively. Furthermore, they found that Sb levels decreased to the background level within 10 m from road edges. This was attributed to the association of Sb with larger particles, which can less easily be spread over large areas than fine particles. The dominance of brake linings as an Sb source was further proven by high correlations with magnetic susceptibility.

The mobility of Sb in soils and sediment is affected by factors including total Sb content, pH, redox potential, and presence of sorbents. As recently reviewed by Wilson et al. (2010), Sb mainly resides with oxides of Al, Mn, and Fe or is attached strongly to organic matter under natural soil conditions. However, due to the neutral character of $\text{Sb}(\text{OH})_3$ it is more strongly sorbed than the anionic $\text{Sb}(\text{OH})_6^-$ under neutral and alkaline soil conditions (Johnson et al., 2005). With decreasing pH, the sorption of SbV becomes more significant (Tighe et al., 2005). As a consequence, Sb is rather slightly mobile in soils and sediments under common soil pH conditions. Sequential extraction procedures (SEP) are

frequently used to determine the association of potentially toxic elements with specific phases, such as mineral and organic matter. Although SEPs have several disadvantages (lack of selectivity of reagents, readsorption and redistribution of elements previously solubilized, incomplete dissolution, nonhomogeneity of samples), as summarized by Bacon and Davidson (2008), their merits are more significant overall. They facilitate evaluation of the potential mobility of elements and their environmental accessibility, as well as determination of plant-available fractions (Ettler et al., 2007; Gleyzes et al., 2002; Wang et al., 2011). However, information on Sb fractionation in traffic-affected roadside soils is still lacking.

Based on the above, the scope of this study was to provide detailed information about the spatial distribution patterns of total Sb in roadside soils, with considerably higher spatial resolution than in previous publications. To assess the environmental risk potential of Sb in roadside soils, chemical fractionation was conducted by applying SEPs. Further, distribution patterns of several trace metals (such as Cd, copper (Cu), Pb, and Zn) were examined to identify distribution patterns related to different emission sources, in order to confirm that brake linings are a major source of Sb. To achieve this, we studied roadside soils along an arterial road in Cologne (Germany) along five transects.

2. Material and methods

2.1. Sampling site, sampling, and sample preparation

The sampling site was located on the east side (leeward) of Berrenrather Street in the “Äußerer Grüngürtel” in south Cologne (Klettenberg and Raderthal), between “Militärstraße” (L34/B51) and the federal highway A4 (Fig. 1a). A traffic light is situated roughly 400 m north, with this regularly resulting in the formation of traffic jams that extend into town. Average daily traffic on the “Berrenrather Straße” was estimated at about 9000 vehicles (Pollok et al., 2011). Sampling was conducted along five transects perpendicular to the road, at intervals of 10 m. Each transect consisted of seven sampling points, including directly at the edge of the road, and at 0.25, 0.5, 1, 2.5, 5, and 10 m distances from the road's edge (Fig. 1b). As maximum distance 10 m was chosen as other studies have showed that traffic-related contamination has decreased down to background values at this distance to the road. At each point, samples were recovered using a percussion corer (Cobra TT, Atlas Copco, Stockholm, Sweden); cores were then divided in the laboratory into depth layers of 0–5, 5–10, 10–20, and 20–30 cm (with no compression observed).

All samples were dried at room temperature and subsequently sieved to a size fraction <2 mm. Subsamples were ground to analytical grain size with a grinding jar and balls of yttrium-partially stabilized zirconium oxide (MM400, Retsch, Haan, Germany).

2.2. Soil characterization

2.2.1. General soil properties

Approximately 1 g of each sample was weighed into a flask and spiked with 5 mL of 0.01 M calcium chloride (CaCl_2) solution. Samples were shaken for 1 h in a horizontal shaker (3006, GFL, Burgwedel, Germany) at 200 rpm. The suspension was allowed to settle for 1 h, with the pH value of the suspension then measured potentiometrically using a calibrated glass electrode (Primatrod, Metrohm, Herisau, Switzerland).

Particle-size distribution was determined using three bulk samples collected between transects III and IV at distances of 0.5–1, 5, and 10 m from the road. We conducted wet sieving (for the sand fraction) and sedimentation using the pipette sampling technique

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