



Pseudo-total antimony content in topsoils of the Berlin Metropolitan Area

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Received: 9 March 2020 / Accepted: 27 July 2020 / Published online: 4 August 2020
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Abstract

Purpose Sb is a metalloid that naturally occurs in traces in the Northern German Lowland Area, only. Its frequent and still growing demand for industrial purposes and its release during coal combustion and by vehicular emissions lead to an enrichment of Sb in topsoils. Numerous analyses on heavy metals have been conducted in the urban environment so far, but although Sb can be ecologically harmful and potentially carcinogenic, only few studies on Sb in soils were carried out.

Materials and methods Due to the formation of anthropogenic soils by men, especially in the course of industrialization and after World War II, more than 50% of the Berlin soils consist of anthropogenic material like redeposited natural material, debris, waste, or ashes. This composition of soils of the Berlin Metropolitan Area can function as a model for other metropolitan regions of Central Europe. In the urban and peri-urban area of Berlin, analysis of more than 900 topsoil samples has been performed measuring the content of 12 heavy metals and metalloids (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, and Zn). As a reference for the natural environment, soil profiles of typical parent rock material have been investigated taking also the regional (0.3 mg/kg), the local background value (0.61 mg/kg), and the baseline value (0.07 mg/kg) for Sb into account.

Results By doing so, we could show the spatial distributional pattern of Sb in the Berlin Metropolitan Area and statistically evaluate our results in dependency of land-use, parent material, and soil parameters such as organic carbon content and pH. Thereby, we could prove an average enrichment two to six times over the regional background value. Median Sb content is very low in forest topsoils (0.54 mg/kg) and reaches its maximum in roadside soils (1.75 mg/kg). Technogenic materials, vehicular emissions, industrial processes, and (former) land-use are the predominant factors for Sb enrichment and distribution in the study area. Some single samples show an enrichment of up to 600% of the regional background value for topsoils.

Conclusion Our study revealed that the Sb content in the Berlin Metropolitan Area is elevated compared to natural environments. Furthermore, we could demonstrate that Sb is a previously neglected key pollutant, specific to metropolitan areas. Due to the high environmental relevance, further Sb data from selected investigated spaces in other metropolises and specific land-use types are needed to assess the potential environmental risk of Sb in metropolitan areas.

Keywords Trace metals · Urban geochemistry · Pollution index · Technogenic soils · Antimony (Sb) · Urban structure type

Poster Presentation held at SUITMA 10 conference, 16 June 2019–21 June 2019, Seoul, Korea

Responsible editor: Stefan Norra

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11368-020-02742-9>) contains supplementary material, which is available to authorized users.

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1 Introduction

1.1 Antimony—general properties and natural occurrence in Central Europe

Antimony (Sb) is a metalloid trace element of the 15 IUPAC group that is, depending on the environment, occurring in a tri- (Sb(III)) or pentavalent (Sb(V)) state (Filella et al. 2002, 2009; Wilson et al. 2010). Sb has two stable isotopes that are distributed with 57.21% (¹²¹Sb) and 42.79% (¹²³Sb), respectively (Chang et al. 1993). In soils with oxic conditions, the pentavalent antimonate (Sb(OH)₆⁻), usually adsorbed to iron (Fe), aluminum (Al), or manganese (Mn) hydroxides, is

considered to be the dominant Sb species (Clemente 2012; Leuz et al. 2006; Verbeek et al. 2019). Nevertheless, trivalent $\text{Sb}(\text{OH})_3$, bound to soil organic matter, may be also present in organic-rich acidic soils (Buschmann and Sigg 2004; Wilson et al. 2010). In topsoils of Germany, geogenic Sb is mainly present in soils emerged from pre-Quaternary magmatic and metamorphic rocks of the low mountain ranges (e.g., Harz Mountains, Ore Mountains) (0.83–1.46 mg/kg), whereas in topsoils of Quaternary sediments of the North European Plain, it only occurs in low to very low content (< 0.6 mg/kg). The FOREGS program maps of top- and subsoil Sb content (Salminen et al. 2005) clearly show that bipartite distribution pattern which extends further across national borders. However, the natural distribution pattern cannot be transferred to the microscale urban environment of the Berlin Metropolitan Area (BMA) with its heterogeneity in terms of parent material, land-use and land-use change, history, and, to a minor amount, geology. In general, anthropogenic input in industrialized countries resulted in an elevated heavy metal content in soils, particularly in urban environments (Demetriades et al. 2010).

1.2 Technogenic and anthropogenic sources of Sb

Especially since the beginning of industrialization, Sb has been enriched worldwide in urban soils, as it is used in many industries (Alloway 2012) and released during fuel and coal combustion (Smichowski 2008). Even in agricultural soils of Germany and Poland, Reimann et al. (2003) assessed top- to subsoil Sb ratios of 1.4 and 1.3, respectively, pointing to anthropogenic and natural Sb enrichment. Since ancient times, a tin-copper-antimony alloy (pewter) has been used for producing metal artifacts, plates, and other tableware (The Pewter Society 2019; Wardas-Lasoń and Garbacz-Klempka 2016). Through smelting processes and mining activities, Sb can be released to the atmosphere as antimony trioxide (Sb_2O_3) (Oorts et al. 2008) and redeposited on plant surfaces or soils. Furthermore, Sb is used in many industrial products such as vehicle brake linings and tires (Hjortenkrans et al. 2007; Varrica et al. 2013), and flame retardants (Zhang and Horrocks 2003). It is also occurring in polyethylene terephthalate (PET) bottles, produced for juices and drinking water (Hansen et al. 2010; Westerhoff et al. 2008). Sb plays a vital role in semiconductor technology and manufacturing industries, as well as the fabrication of paints and batteries. Also, it is an essential alloying agent for lead and copper alloys used in ammunition and projectiles (Filella et al. 2002), so that especially shooting range soils can be heavily loaded with Sb (e.g. Johnson et al. 2005; Okkenhaug et al. 2013). Beyond that, residuals of smelting and combustion processes (slags, ashes) and wastes contain some amount of Sb (e.g. Klemettinen et al. 2019; Miravet et al. 2006; van Velzen and Langenkamp 1996). The elevated Sb content in urban soils is

considered to stem mainly from these (former) technogenic and anthropogenic sources (Online Resource 1). Due to exhausts and abrasion from tires (Földi et al. 2018; Smichowski 2008), the Sb content can be assumed to be generally higher next to roads. Hence, the still growing demand for industrial products and an increasing volume of individual traffic boosts the release of Sb to the urban environment and enhances the enrichment and contamination of anthropogenically influenced urban soils by Sb and other heavy metals.

In Metropolitan areas, some studies (Gómez et al. 2005; Langner et al. 2011) demonstrated an enrichment of Sb in airborne PM_{10} particulate matter and road dust next to busy roads. For ambient air in the BMA, the Sb content in PM_{10} particles ranges from 1.2 to 8.5 ng/m^3 , depending on the location (Langner et al. 2011). Thus, wet and dry deposition of airborne Sb particles subsequently lead to a higher content in urban and peri-urban soils. In the BMA, another main source of a high Sb content exists: debris from World War II (WW II) is present in large parts of the city (Forßbohm 2011; Makki 2015) either as heterogeneous parent material or as a component in other parent rock for soil formation. This material (e.g., bricks, concrete, roof tiles, and masonry) contains an elevated amount of heavy metals (Mekiffer 2008) from the pre-war period when Berlin was an industrial city as well as residues from WW II house fires and firestorms.

1.3 Environmental risks and toxicological profile

Sb compounds exhibit a high human medical and environmental significance. Antimony trioxide (Sb_2O_3) was declared as a potential carcinogen by the International Agency for Research on Cancer in 1989 (IARC 1989). Generally, trivalent antimonites are more toxic than pentavalent antimonates and organoantimonials (Gebel 1997; He and Yang 1999; Wilson et al. 2010). Despite its toxicity, test, guideline, and precautionary values for Sb in soils are still missing in Germany. In other countries, such as Finland (threshold value: 2 mg/kg, lower guideline value for health risk assessment: 10 mg/kg) or the Netherlands (target value: 3 mg/kg, intervention value: 15 mg/kg), such values for soils were defined (Ministry of the Environment, Finland 2007; Dutch Target and Intervention Values 2000), but the derivation of these values remains unclear. Although investigations on Sb gained more interest during the last decades and studies on its speciation (e.g., Wilson et al. 2010), its bioavailability (e.g., Gál et al. 2007; Pierart et al. 2015), and its environmental risk (e.g., Tschan et al. 2009), as well as its potential threat to human health (Gebel 1997; Sundar and Chakravarty 2010) have been carried out, there is still a lack of information concerning the distribution of Sb in rural and urban environments and its potential risk. The mobility of $\text{Sb}(\text{OH})_6^-$ is increased in alkaline to slightly acidic conditions (Wilson et al. 2010). As anthropogenic and technogenic soils in the BMA

often show pH values in this range (Mekiffer 2008; Makki et al. 2020, this special issue), the mobility of Sb in urban soils can be regarded as higher than in near-natural environments. The enhanced mobility becomes especially relevant, since Sb is a pollutant typical for the urban environment. Therefore, further research is required to gain a broader understanding.

1.4 Geochemical studies in urban environments

Soils in the urban environment can act as sinks or sources for pollutants such as heavy metals and metalloids (HMs) (Alloway 2012; Clark et al. 2006). In a globalized world, a further increasing degree of urbanization and industrialization is projected, especially in rapidly growing cities and metropolises of the Global South (Makki and Köhler 2013; United Nations, Department of Economic and Social Affairs, Population Division 2019). Therefore, we assume that urbanization and industrialization are, and could become, multipliers for the uptake of HMs by soils, especially in countries with low environmental standards. In soils of urban, industrial traffic, mining, and military areas (SUITMAs) (Burghardt et al. 2015), where the input of HMs by industrial production, traffic and combustion processes, or technogenic materials is ubiquitously (Alloway 2012), numerous surveys on soil HM content have been carried out (e.g., case studies summarized in Ajmone-Marsan and Biasoli 2010). Most of the cited studies deal with key pollutants such as lead (Pb), cadmium (Cd), zinc (Zn), and copper (Cu). In comparison with studies on these HMs, investigations on antimony (Sb) are rather sparse.

In Germany and Europe, geochemical studies that include Sb have been carried out in several cities (Online Resource 5), but especially in China, that is by far the largest producer of antimony ores (United States Geological Survey 2019), a considerable number of studies on Sb in urban and rural soils as well as in soils of mining areas have been realized (e.g., Cheng et al. 2014; He et al. 2012; Wan et al. 2018). These studies showed that the Sb content in soils of urban areas can reach mean values of up to 6.78 and mg/kg (Cheng et al. 2014; He et al. 2005). Since currently only a few studies on Sb and its fate in urban soils are available, we believe it is mandatory to conduct geochemical investigations also in heterogeneous urban and metropolitan areas. In particular, the various physical and chemical soil properties due to anthropogenically induced alterations and land-use history of urban soils should be considered.

1.5 Objectives

The primary objective of our study was to close the still existing knowledge gap about the spatial distribution of Sb in the BMA as well as its relation to selected soil parameters. In contrast to the previous works in the BMA of Birke and Rauch (1994, 1997, 2000), we measured the *aqua regia*-soluble HM fraction

(“pseudo-total HM content”) and not the total Sb content which has been assessed by x-ray fluorescence (XRF) analysis. This method, that does not dissolve the soil matrix completely, is the standard method for measuring the HM content according to the German Soil Protection Directive (BBodSchV 1999) and measures the HM content of soils which can be supplied by the respective substrate in the short and long term. In international literature (e.g., Greinert 2015), this fraction is also cited as sub-total HM content. In metropolitan areas with either residential and industrial land-use, the Sb content is assumed to be generally higher due to either technogenic or anthropogenically relocated parent material as well as high input by diffuse or identifiable anthropogenic sources. On the other hand, natural soils in the peri-urban area, with only little anthropogenic impact, should show a low Sb content close to local and regional background values. In our study, we used data from 901 topsoil samples (0–20 cm) and six reference profiles to determine the pseudo-total HM content in the BMA and classified the results by urban structure types (USTs). Furthermore, we assessed the degree of contamination by calculating and evaluating different pollution indices.

2 Material and methods

2.1 Study area

The Berlin/Brandenburg Metropolitan Area (BMA) is one of 11 Metropolitan Areas in Germany with an area of approximately 30,546 km² (further information see: www.berlin-brandenburg.de, in German). In our study, we focused on the urban and peri-urban area (891 km²) within the city of Berlin’s administrative borders. Berlin is located in the young morainic landscape of the North German Plain next to the rivers Havel and Spree. Residential, commercial, and industrial areas, as well as urban infrastructure (streets, railway lines, etc.), comprise 58.9% of the city area. Urban green spaces and other close to nature areas (17.6%), forests (17.5%), lakes, and rivers (6.0%) account for 41.1% of the area (Senate Department for Urban Development and Housing Berlin 2016a). Soils in the near-natural environment of the BMA consist of Late Pleistocene and Holocene sediments (further information about the geological situation can be found in the soil section of the Berlin Environmental Atlas: https://www.stadtentwicklung.berlin.de/umwelt/umweltatlas/edinh_01.htm). In the urban and peri-urban landscape of the BMA, only 47% of the soils are build-up by these natural sediments. Soils of the study area frequently (53%) consist of anthropogenically redeposited natural material or technogenic substrates (Makki 2015) such as building rubble, debris from WW II, or construction sands (e.g., for road construction). These parent materials show a heterogeneous physical and chemical composition and are extensively distributed

in the BMA. Their origin and their compounds, as well as their physical and geochemical soil properties, have a decisive impact on the distribution of HMs in the BMA (Mekiffer 2008; see also Makki et al. 2020, this Special Issue, under review). Surveys from other SUITMAS in urban areas of Germany and the world (e.g., Helmes 2004; Hiller and Meuser 1998; Holland 1996; Meuser 2010 and references therein) show that technogenic materials are common in metropolitan environments. Therefore, it could be possible to transfer the findings on HM distribution obtained in this study to other urban and metropolitan regions. As especially Central European metropolitan regions share their history, the BMA can function as a role model for other highly urbanized areas.

2.2 Field methods

Between 2016 and 2019, we collected 305 terrestrial topsoil samples in the BMA in dependency of Urban Structure Type (UST). We preferred this methodological approach (irregular sampling) to a grid-like network over the urban area because we were able to demonstrate that the variance of soil properties (pH, humus content, calcium carbonate content) within the single USTs is minor as between different structure types (Table 2). UST of our sampling sites has been classified and assigned according to the Urban Structure map of Berlin (Senate Department for Urban Development and Housing Berlin 2016b) as well as the Map of Soil Associations (Senate Department for Urban Development and Housing Berlin 2018). For study sites that did not match a specific UST or where no UST is defined, classification was performed manually according to the code list of the Senate Department for Urban Planning and the Environment Berlin (2016). In total, 15 USTs have been included in our study (Table 1, further information and

description of USTs and IDs see: Senate Department for Urban Development and the Environment Berlin (2016) (in German with illustrations)).

For topsoil samples, we excavated a small soil plot of 30 × 30 cm and 30-cm depth and cleaned the walls carefully with a plastic spatula. Primarily, mixed topsoil samples (up to 20-cm depth) from all sides of the plot were collected. Typically, these samples were “A” horizons, but on ruderal sites with small A horizons also natural or anthric/technic material from the subsoil has been collected. Additionally, we excavated six “uncontaminated” soil profiles up to a depth of 2 m to calculate the local geochemical background values (LGB). For further evaluation of the Sb content, we included more than 600 archived topsoil samples from previous mapping projects of Humboldt-Universität zu Berlin, giving a total of 907 analyzed soil samples (Online Resource 2a-g). In the inner-city area, sampling density was about 1 sample per km².

2.3 Laboratory analyses and sample preparation

Laboratory analyses comprised the assessment of the topsoil content of 12 HMs (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Zn), the determination of the humus content, pH value, and CaCO₃ content using standardized methods as well as grain size analysis. The particle size distribution has been determined by Laser Diffraction (LS 13320, Beckman-Coulter, Brea, USA) and evaluated according to soil textural classes as provided by FAO (2006). Soil pH has been measured in a 0.01 M CaCl₂ solution (1:2.5 soil-to-solution ratio) using a glass electrode (HI-1230, Hanna Instruments, Germany) (DIN EN 15933:2012–11). The calcium carbonate (CaCO₃) content has been determined using the volumetric Scheibler method (DIN EN ISO 10693:2014-06). Furthermore, we quantified the humus

Table 1 Urban structure types (USTs) according to the code list of the Senate Department for Urban Development and the Environment Berlin (2016)

Urban structure type	ID	Comment
Residential areas	WOZ 10	
Mixed development	WOZ 21	
Commercial and industrial areas	WOZ 40	
Public service and other special uses	WOZ 50	
Fallow lands	Typ 57	Encompasses GRZs 171, 172, and 173
Roadside soils	WOZ 80	
Other traffic areas	–	Encompasses types 91, 92, 94, and 99
Forests	GRZ 100	
Grassland	GRZ 121	
Agricultural areas	GRZ 122	
Parks and other urban green spaces	GRZ 130	
Promenades and city squares	GRZ 140	
Cemeteries	GRZ 150	
Allotment gardens	GRZ 160	
Horticulture	GRZ 200	

content by the loss-on-ignition-method (LOI) at 420 °C. Detailed descriptions are attached (Online Resource 3).

2.4 Pseudo-total heavy metal content

The pseudo-total HM content has been determined by *aqua regia* digestion according to DIN EN 16174:2012-11 (2012). Therefore, 1 g of fine soil has been put into crucibles, and the organic substances have been incinerated by LOI at 550 °C (preheat: 90 min, heating: 30 min). Subsequently, the soil samples have been transferred to 50-ml Erlenmeyer flasks and, together with a method blank, digested in a 3:1 *aqua regia* solution (6 ml 38% HCl, 2 ml 68% HNO₃, heating for 2 h at 115 °C). Following cooling, the samples have been diluted to 50 ml with 2 M HNO₃ and filtered through folded filters (Rotilabo®, Type 601P, Carl Roth, Karlsruhe, Germany). The measuring of the filtrates has been performed by ICP-OES (iCAP 6300 Duo, ThermoScientific, Waltham, USA). Quality check (QC) has been carried out after every tenth sample using respective standard solutions. The method for the assessment of the limit of detection (LOD) and the limit of quantification (LOQ) is described in detail in Online Resource 3.

2.5 Statistical evaluation

Median Sb values have been calculated for each classified UST as well as for the total dataset. Furthermore, bivariate correlations of Sb with other HMs have been determined for every UST with at least 10 samples (Table 3). Beforehand, Shapiro-Wilk-test was used to test normality. As normality was not given for most of the analyzed HMs, bivariate correlations have been determined by using Spearman's rank correlation coefficient (ρ). We performed all statistical analyses with Open Source Software RStudio Version 1.2.1335 (RStudio Inc., Boston, MA, USA).

2.6 Calculation of background values

Calculation of standard pollution indices is a common tool to examine whether an element is enriched, compared to the reference element content of the same or other elements in the upper continental crust or background. Simple and more sophisticated indices can be determined to investigate the soil quality or the potential ecological risk (Kowalska et al. 2018). For all these indices, selecting a suitable background value is the essential decision for the interpretation of the data.

In the BMA, local background values (LGB) for Sb are missing. Therefore, we decided to assess the median of the topsoil layer (A horizon) and the baseline value (C horizon) of six “undisturbed” forest soil profiles (soil texture: sandy loam and loamy sand) in the Western and Northern districts of Berlin. In addition to LGB, we utilized the regional

geochemical background value (RGB) for sandy topsoils and the baseline value (BV) as provided by LABO (2017).

2.7 Pollution index and contamination factor

To assess the pollution or contamination level of topsoils with HMs (especially Sb) in the BMA, we determined the Single Pollution Index (PI) (Chen et al. 2005; Kowalska et al. 2018) and the contamination factor (C_f) (Håkanson 1980; Abraham and Parker 2008) for each sample as follows:

$$PI = \frac{c_{\text{sample}}}{c_{\text{RGB/LGB}}} \quad (1)$$

$$C_f = \frac{c_{\text{sample}}}{c_{\text{BV}}} \quad (2)$$

where c_{sample} is the element content in the investigated topsoil and $c_{\text{RGB/LGB/BV}}$ are the respective reference values. We determined PI using both RGB and LGB and for the calculation of C_f the respective BV for sandy soils (C horizon) (LABO 2017), instead of the pre-industrial levels for lake sediments as cited by Håkanson (1980). Modified degree of contamination (mC_d) (Abraham and Parker 2008) has been assessed to determine the overall degree of contamination with nine analyzed HMs. mC_d has been assessed and classified using a slightly modified variant of the original formula of Abraham and Parker (2008):

$$mC_d = \frac{(\sum_{i=1}^{i=n} PI_{\text{RGB}}^i)}{n} \quad (3)$$

where PI_{RGB} is the sum of all single element RGB pollution indices (instead of BV) and n is the number of HMs analyzed.

All pollution indices have been classified as summarized in Kowalska et al. (2018).

3 Results and discussion

3.1 Limit of detection and limit of quantitation

Measurement of 28 method blank samples by ICP-OES yielded an average Sb concentration of 0.001614 mg/l and a standard deviation (σ_{MB}) of 0.000638 mg/l. Therefore, LOD is 0.002171 mg/l which equals 0.11 mg/kg Sb (50 ml solution). While the spiked samples with concentrations of 0.004 and 0.005 mg/l exhibit low recovery rates (40.9 and 26.0%, respectively) due to matrix effects, the spiked samples with concentrations between 0.006 and 0.008 mg/l show acceptable recovery rates < 20% (3.7, 15.5, and 16.2%, respectively). For Sb concentrations > 0.006 mg/l, the average precision of all replicates is < 20%. Consequently, LOQ has been set to 0.006 mg/l equal to 0.3 mg/kg. In total, 57 samples, mostly in forest soils, exhibit a low Sb content < LOQ but > LOD.

3.2 General soil physical and soil chemical parameters

The BMA is a heterogeneous mosaic in terms of soil and land-use type as well as parent rock material (Makki 2015; Senate Department for Urban Development and Housing Berlin 2018). Hence, the composition of the soil and its properties can change considerably within short distances and between USTs. Especially the multitude of anthropogenic and technogenic materials occurring in the urban soils of the BMA has a tremendous impact on general soil properties (Table 2) and, consequently, the distribution of HMs. Built-up anthropogenic and technogenic soils have often been treated with amendments such as peat, ashes, and sewage sludge (Makki et al. 2011), resulting in altered physical and chemical soil parameters. In natural, peri-urban environments, the effect of technogenic materials on soil parameters, and their variance decreases, but during sampling, we occasionally found illegal waste dumping sites and technogenic materials (bottom ashes, bricks, and slags from former times) in forests.

3.3 Sb content in the Berlin Metropolitan Area

Our geochemical survey in the BMA based on 907 topsoil samples is one of the most detailed studies on the Sb content in urban areas so far. Averaged Sb content of the six investigated remote sites (soil texture: loamy sand) yielded the LGB of 0.61 mg/kg Sb, which is approximately 2 times higher than

the RGB (0.30 mg/kg) for sandy forest topsoils in NE Germany (LABO 2017). This observation implies that the topsoil samples of the remote sites in the BMA are most likely affected by Sb input from anthropogenic sources. Due to the low natural occurrence of Sb in the local parent rock, BV is close to zero (0.07 mg/kg for sandy soils) (LABO 2017).

Irrespective of UST, our analysis yielded a median of 0.96 mg/kg Sb, which is approximately 1.3 (LGB) to 3 (RGB) times the respective background value. Twenty-one samples, reported as < LOD, have been intentionally set to zero. In general, Sb contents, as well as other HM contents, reflect the urban-rural gradient with decreasing loads in the suburban area, but regularly locally elevated contents of Sb can be associated with specific land-use types or technogenic material. Furthermore, former land-use plays a decisive role in Sb content and distribution in the BMA. This becomes obvious, as our study shows that Sb is mainly enriched in the central, densely populated districts of Berlin, the so-called Wilhelminian Belt (Fig. 1), and along Spree river. The city center has been developed and urbanized in the 19th and early twentieth century when Berlin was one of the most industrialized cities across the globe. Due to industrialization and the burning of fossil fuels, such as briquettes and coke, these districts generally show a higher HM content than the peri-urban suburbs, which have been subsequently urbanized after 1920 and WW II. Therefore, an increased Sb content occurs more likely along the radially designed axes of transportation

Table 2 Median, minimum, and maximum values for Sb ($N=907$) and range of general soil parameters, classified by urban structure type (UST)

UST ^a	N	Sb [mg kg ⁻¹]			pH [CaCl ₂] (median)	Humus [%] (median)	CaCO ₃ [%] (median)
		Min	Med	Max			
Res	45	0.14	0.89	4.53	4.9–7.6 (6.3)	0.4–7.7 (3.2)	0–4.1 (0.4)
Mix	10	0.72	6.41	80.32	5.3–7.7 (6.4)	1.5–33.7 (3.7)	0.1–3.1 (0.8)
Ind	44	0.15	1.50	173.34	5.9–8.2 (6.8)	1.0–11.4 (3.4)	0.1–10.0 (1.3)
Pub	26	n.d.	0.85	28.47	4.2–8.3 (6.6)	0.7–19.0 (4.0)	0–4.1 (0.3)
Fal	119	n.d.	0.66	22.42	3.9–7.7 (6.4)	0.3–17.9 (3.7)	0–19.0 (0.2)
Rss	96	0.21	1.79	11.19	5.3–7.7 (6.6)	0.8–12.1 (4.6)	0–4.0 (0.7)
Otc	5	0.44	1.27	4.29	5.9–7.7 (6.8)	1.4–12.2 (4.1)	0–3.6 (0.9)
For	163	n.d.	0.54	55.05	3.0–6.8 (3.9)	0.4–58.5 (2.9)	0–3.4 (<0.1)
Grs	8	0.42	1.19	3.91	3.9–7.7 (5.3)	1.9–55.0 (4.7)	0–13.3 (0.1)
Agr	54	n.d.	0.75	22.42	4.4–6.7 (5.3)	1.1–7.8 (1.9)	0–2.5 (<0.1)
Prk	295	n.d.	1.13	22.71	4.0–7.8 (6.3)	0.1–27.7 (4.2)	0–8.8 (0.4)
Csq	18	0.68	1.38	9.22	5.8–7.6 (6.8)	2.1–12.4 (5.0)	0–1.9 (1.0)
Cem	5	n.d.	1.33	2.99	5.0–7.1 (6.2)	1.3–9.5 (5.2)	0–0.5 (0.2)
Alg	14	0.12	1.21	9.41	4.5–7.6 (6.7)	1.8–11.3 (4.6)	0–6.8 (0.4)
Htc	5	0.11	2.38	14.20	6.0–7.3 (7.0)	3.5–5.7 (4.4)	0–3.7 (0.9)
total	907	n.d.	0.96	55.05	3.0–8.3 (6.2)	0.1–58.5 (3.8)	0–19.0 (0.1)

^a Abbreviations for urban structure types: *Res*, residential areas; *Mix*, mixed development; *Ind*, industrial areas; *Pub*, public service and other special uses; *Fal*, fallow areas; *Rss*, roadside soils; *Otc*, other traffic areas; *For*, forests; *Grs*, grassland; *Agr*, agricultural areas; *Prk*, parks and urban green spaces; *Csq*, promenades and city squares; *Cem*, cemeteries; *Alg*, allotment gardens; *Htc*, horticulture

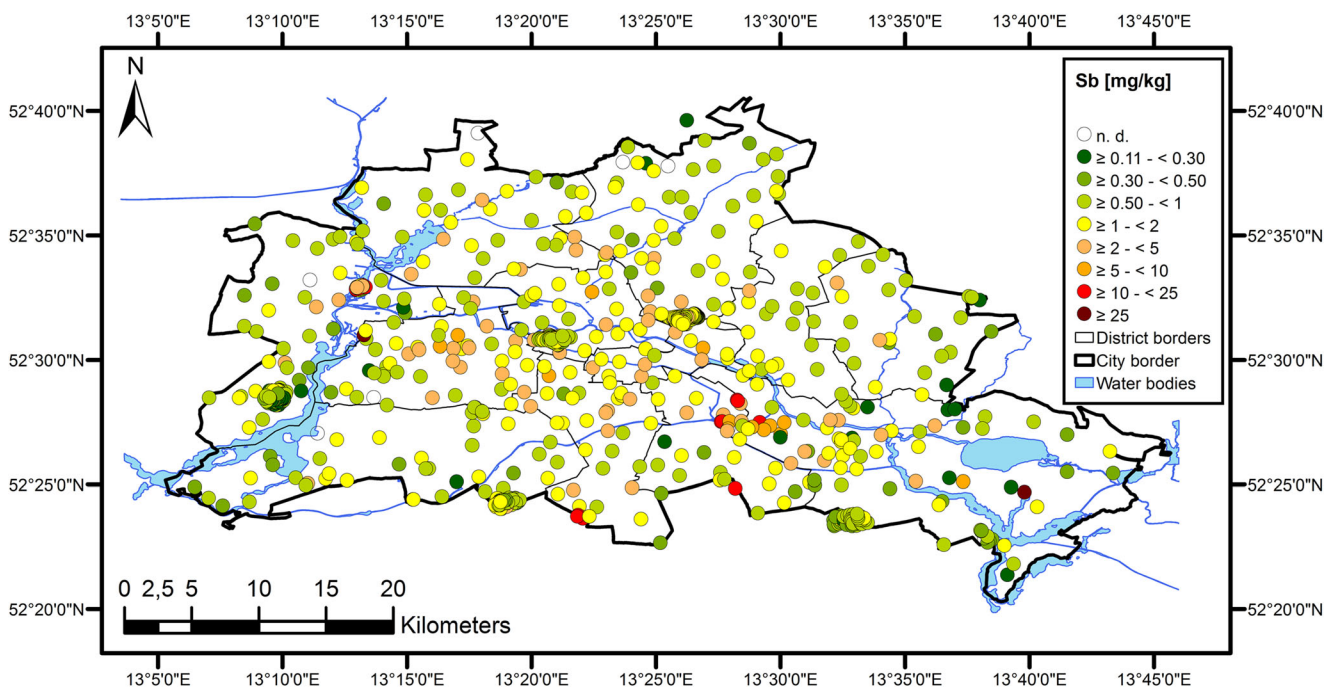


Fig. 1 Distributive map of Sb content (in mg/kg) in the BMA based on 907 topsoil (0–20 cm) samples

(streets, channels, railway lines) as well as in residential and industrial areas of the Wilhelminian period (Fig. 1). Other substantial sources for Sb and other HMs are the war debris from WW II and building rubble, that have been extensively distributed in the inner city and occur in parks and city squares, and some residential areas. This material has been incorporated into the soil, used for landfills (e.g., bomb craters, trenches), leveling of the surface, and was raised intentionally to dumping sites or piles (Forßbohm 2011; Makki 2015; Makki and Thestorf 2015).

Calculation of median, minimum, and maximum values for 15 USTs of the BMA revealed the heterogeneity of soil physical and soil chemical parameters and the Sb content in the urban and peri-urban environment (Table 2 and Fig. 2). Frequently, there is an extraordinary variance even within some of the investigated urban structure types, which is typical for urban soils in the BMA.

3.4 Sb content classified by UST

In our view, the classification of sampling sites to USTs is essential to understand the spatial distributional pattern of HMs in urban areas. For most of the investigated USTs, the enrichment of Sb can be explained by parent material, the former and current land-use, and management practices. Generally, observed that the more sources of contamination affect the topsoils, and the closer the sampling location to a point or linear source, the higher is the Sb enrichment. However, the sources of contamination vary between the respective USTs. By our study, we were able to prove that the

median Sb is very low to low in topsoils of forests ($N=163$) and fallow lands ($N=119$) (0.54 and 0.66 mg/kg, respectively). Both USTs are usually unaffected by direct anthropogenic HM input related to technogenic materials. Hence, they show an Sb content below or close to LGB and RGB. However, the slightly elevated median Sb compared with RGB indicates, that these USTs are also affected by HM deposition from distant sources. Even though forest soils are typically not polluted, some samples show a very high Sb content, such as one single sample on a former shooting range (55.05 mg/kg). Fallow areas with a low Sb content are typically on the outskirts of the BMA. Though, some parts of the former Berlin Wall border strip are still regarded as barren land, which is an immediate outcome of military use between 1961 and 1990. These soils have been strongly anthropogenically transformed by regular plowing and harrowing. Furthermore, they have been kept free from vegetation by pesticides. Some sections of the southern Berlin Wall border strip were part of the sewage farms or adjacent to them (Makki et al. 2010, 2011), so that these samples show a high Sb enrichment, even in subsoil horizons.

Topsoils of residential areas ($N=45$), “public areas and other special uses” ($N=25$) as well as agricultural areas ($N=54$) show a moderate and slightly higher Sb content (median: 0.89, 0.85, and 0.75 mg/kg, respectively) compared with LGB. Taking the RGB into account, the median Sb is 2.5 to 3 times elevated. Residential areas under investigation that have been build-up after WW II, which are located at some distance from the roads and other contamination sources, or are situated on more naturally designed Anthrosols and Technosols

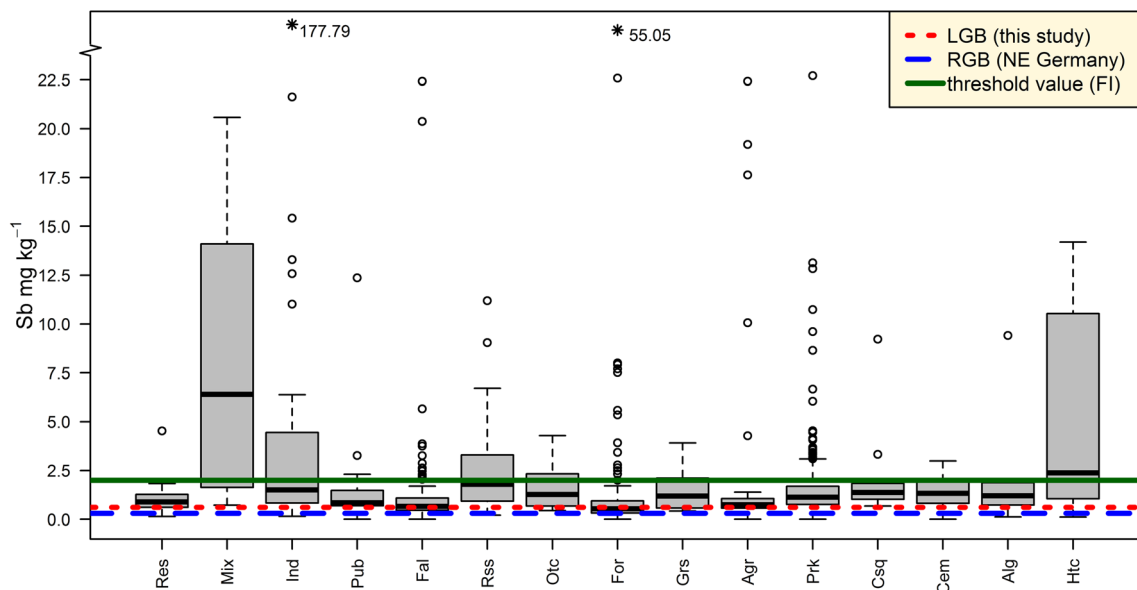


Fig. 2 Pseudo-total Sb content in mg/kg in topsoils grouped by urban structure type, local background value (LGB): six uncontaminated reference profiles in the Berlin Metropolitan Area, regional background value

(RGB), NE Germany LABO (2017), threshold value as established by the Ministry of the Environment, Finland (2007)

show a lower Sb content than those from pre-war times. On the other hand, soils in agricultural areas are slightly enriched with Sb and other HMs, most likely due to the treatment with fertilizers or pesticides, which may contain specified amounts of ashes or sewage sludge (DüMV 2012). Our samples from farmland sites along the former border strip of the BMA, which have been used as sewage farms (Senate Department for Urban Development and Housing Berlin 1992; Birke and Rauch 2000), exhibit a very high Sb and HM content (As, Cd, Cr, Cu, Ni, Pb, Zn).

Topsoils in parks and urban green spaces ($N=295$) and allotment gardens ($N=14$) show an enrichment with Sb (median: 1.13 and 1.21 mg/kg, respectively) and other HMs, usually Cu, Ni, Pb, and Zn. Occasionally Fe and Cr are elevated, compared with RGB. As stated before, this elevated HM content in parks of the BMA is attributed to extensively distributed debris from WW II. Our studies in the BMA revealed that some of these park soils consist of contaminated technogenic material only, such as parts of Volkspark Friedrichshain and Tiergarten (Bischoff 2018a; Bischoff 2018b). In the BMA, there are several other examples for parks that have been anthropogenically constructed and consist of either waste or war debris (Humboldthain, Insulaner) (Senate for Urban Development and Housing Berlin 2018).

A remarkable median Sb content in the BMA (4.6 to 6 times the RGB) has been detected in topsoil samples from roadside soils ($N=96$) (median: 1.79 mg/kg), promenades and city squares ($N=18$) (median: 1.38 mg/kg), and industrial areas ($N=44$) (median: 1.50 mg/kg). Sb enrichment in these topsoil samples can be primarily attributed to the input of roadside dust (e.g., abrasion from tires and brake linings)

(Hjortenkrans et al. 2007), industrial emissions, and technogenic materials. Along busy roads, vehicular emissions are the major source of pollution, resulting not only in an Sb enrichment but also in a very high content of other traffic-related HMs (Cu, Pb, Zn). We could observe that near the A 100 highway and highly frequented roads, the Sb content can be as high as 11.2 mg/kg soil. A very high correlation coefficient with Cu, particularly near traffic lights, points to emissions from brake linings as a primary source for Sb in roadside soils (Földi et al. 2018). The spatial distributional pattern of Sb along roadsides (Online Resource 4) shows that the highest Sb content is located near the road. Vegetation, hedges, and buildings hinder the extensive spread of HMs beyond the first 100 m from the roadway. Promenades and city squares are often affected by human impact. Like roadside soils, city squares are next to the streets where the deposition of roadside dust can be high. Therefore, especially the samples adjacent to roadsides show a high Sb content. Besides, the artificial design of city squares conditions a high humus content and favorable pH values (~ 5.5 – 6.5) that allow the binding of Sb(III) to humic acids (Buschmann and Sigg 2004). Topsoils in old industrial areas that already exist since the main phase of industrialization (~ 1880 – 1930), such as Eiswerder Island or Schöneweide, yield an even higher Sb content up to 173.33 mg/kg (~ 580 times the RGB). As the accessibility to industrial areas was limited, we took 16 of 44 samples on Eiswerder Island, which may impact the median. The high Sb content can be attributed to the extreme enrichment of metal scrap, glass slags, copper slags, and ashes in the case of Eiswerder as well as to the non-ferrous smelters and the production of batteries in Schöneweide (Birke et al. 1992). In

one soil profile on Eiswerder Island, we could identify technogenic materials up to a depth of 120 cm. At this location, there is a high environmental risk potential because the groundwater table is less than 1 m below the contaminated soil layer. Topsoils of mixed areas ($N=10$) and horticultural areas ($N=5$) show the highest medians (6.41 and 2.38 mg/kg, respectively) of our case study. Both structure types should not be regarded as representative for the BMA as the samples could be taken in two very restricted study areas only.

Our research shows that topsoils in the BMA are enriched with Sb and various other HMs. These results are consistent with other geochemical surveys conducted in the BMA (Birke and Rauch 1994, 1997, 2000; Birke et al. 2011) and study areas worldwide (Online Resource 5). In total, our research reveals that 18.2% or 11.7% of all samples ($N=907$) exceed the Finnish threshold and the Dutch target value, respectively. These sampling points are usually located near roadsides, in industrial areas (e.g., Schöneweide), and areas for public service. In 3.0% or 1.7% of all cases, the respective guideline value for health risk (FI) and the intervention value (NL) are surpassed (Online Resources 6 + 7). As no guideline values are currently present for Sb in Germany, the assessment was based on the available values from Finland and the Netherlands (cf. Section 1.3).

Compared to the previous studies, our median value (0.96 mg/kg) is approximately one-third of the weighted average (2.7 mg/kg) for the city area, as reported by Birke et al. (2011). Our result can be explained by several factors: First, *aqua regia* digestion (pseudo-total content) dissolves lower amounts of the analyte than a complete dissolution (total content) (Santoro et al. 2017). According to a comparative study, which was carried out on 19 European soil samples, only 53% of the total Sb content is dissolved by *aqua regia* digestion (Taraškevičius et al. 2013) in comparison with XRF. Second, for a methodological comparison, the selection of sampling sites in a heterogeneous urban landscape is crucial. In a metropolis like Berlin, where soil properties change within short distances, the determined values can be very strongly influenced by the site conditions. Finally, and despite a high affinity for organic substances, Sb may already have been leached into the subsoil. However, this requires further investigations on subsoil samples, speciation, and the binding characteristics of Sb in urban soils.

As several factors may play a role, a simple comparison between the medians of an entire region may not be meaningful as it does not provide us with any additional information about the spatial distribution or the potential ecological risks of Sb in the BMA. Only by categorizing the samples of the BMA into 15 USTs (Table 2), we were able to demonstrate that the Sb content is subject to substantial variations between the individual sites and USTs. Urban soil sampling and determination of HM content are susceptible to a lot of human-induced influences, starting with the heterogeneity of the

anthropogenically relocated materials and built-up soils. To reduce bias in assessing HM content and to cover an entire city area, often a regular cell grid irrespective of UST is used to reduce the impact of over- or underrepresented land-use types or a high amount of samples in a specific location (Cheng et al. 2014). However, as USTs do not occur in equal proportions across a city area, the number of representative samples for a single USTs varied and for some of them, only a low number of samples (<10) could be achieved. These USTs need further investigation. As single samples for a large park or forest area may bias the median, we based our study not only on evenly distributed data. Some study areas (Online Resources 2c-g and 4) with representative soil parameters for the BMA have been investigated intensively to evaluate the spatial distribution of Sb within these USTs. These areas have been studied as a function of determining factors such as closeness-to-roads, changes in the parent material, and soil parameters (Online Resource 2c-g and 4). This is necessary to assess the range of the Sb content within the respective USTs, and also to monitor future changes.

In our view, a reliable evaluation of the spatial distribution, the soil pollution level, potential sources, and risk assessment of Sb is only feasible by the subdivision according to USTs, and regarding the respective soil properties of the investigated sites as performed in this and other studies (e.g., Fordyce et al. 2012; Greinert 2015; Horváth et al. 2015). This approach also complies with the requirements of the German Soil Protection Directive (BBodSchV 1999), which provides an assessment of the environmental and health risk of the HM content according to land-use categories, among others. Currently, a lot of sampling patterns, extraction methods, and analytical standards exist. Therefore, we advise to develop a standardized method for geochemical mapping in urban areas to facilitate a comparison between different studies.

3.5 Statistical evaluation

Spearman rank correlation shows high positive correlation coefficients of Sb with humus (Table 3), especially in topsoil samples of forests, parks, roadside soils, and allotment gardens ($\rho = 0.63, 0.60, 0.60,$ and 0.59 respectively). As these samples contain a very high humus content, we assume, that airborne Sb(III) (e.g., from industrial emissions) forms stable organometallic complexes with functional groups of soil organic matter. As other authors (e.g., Buschmann and Sigg 2004; Johnson et al. 2005; Lewińska et al. 2018) stated, we think that in these USTs, organic substances could be the principal driver for fixating Sb, but according to our knowledge, no specific analyses on Sb binding mechanisms to (technogenic) organic or inorganic substances in urban environments have been carried out, yet. Between pH value and Sb, we observed weak negative correlations in most of the USTs that consist of technogenic material and exhibit pH

Table 3 Spearman rank correlation coefficients of Sb with pH value, soil organic matter content, and 11 heavy metals and metalloids, grouped by urban structure type, abbreviations see Table 2

UST	N	Humus	pH	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Res	45	0.30*	-0.20	0.24	0.38*	0.57**	0.49**	<i>0.61**</i>	<i>0.78**</i>	0.37*	0.33*	<i>0.62**</i>	<i>0.56**</i>	<i>0.62**</i>
Ind	44	0.42**	-0.35**	-0.07	0.50**	0.56**	0.43**	0.18*	<i>0.79**</i>	0.38*	0.34*	<i>0.49**</i>	<i>0.67**</i>	<i>0.77**</i>
Pub	26	0.43*	0.21	0.43*	<i>0.69**</i>	0.43*	<i>0.63**</i>	0.48*	<i>0.74**</i>	<i>0.63**</i>	0.14	<i>0.65**</i>	<i>0.74**</i>	<i>0.61**</i>
Fal	119	0.25**	0.07	0.06	0.42**	0.56**	0.30*	0.37**	<i>0.59**</i>	0.41**	0.17	<i>0.39**</i>	<i>0.66**</i>	<i>0.54**</i>
Rss	96	<i>0.60**</i>	-0.22*	<i>0.64**</i>	<i>0.64**</i>	<i>0.65**</i>	<i>0.74**</i>	<i>0.76**</i>	<i>0.87**</i>	<i>0.79**</i>	<i>0.60**</i>	<i>0.79**</i>	<i>0.76**</i>	<i>0.83**</i>
For	163	<i>0.63**</i>	0.16*	<i>0.56**</i>	<i>0.78**</i>	<i>0.60**</i>	<i>0.59**</i>	<i>0.59**</i>	<i>0.78**</i>	<i>0.73**</i>	0.41**	<i>0.64**</i>	<i>0.82**</i>	<i>0.65**</i>
Agr	54	0.47**	0.09	0.29*	<i>0.65**</i>	<i>0.61**</i>	0.12	0.54**	<i>0.73**</i>	0.39**	0.06	0.57**	<i>0.73**</i>	<i>0.64**</i>
Prk	295	<i>0.60**</i>	0.11	0.38**	<i>0.73**</i>	<i>0.72**</i>	<i>0.63**</i>	<i>0.59**</i>	<i>0.82**</i>	<i>0.65**</i>	0.40**	<i>0.74**</i>	<i>0.78**</i>	<i>0.79**</i>
Csq	18	0.06	-0.40	0.32	<i>0.62**</i>	<i>0.72**</i>	0.43	<i>0.66**</i>	<i>0.72**</i>	0.55*	0.32	<i>0.66**</i>	<i>0.64**</i>	<i>0.75**</i>
Alg	14	0.52	0.49	0.40	<i>0.84**</i>	<i>0.78**</i>	<i>0.74**</i>	0.58*	<i>0.85**</i>	<i>0.87**</i>	0.24	<i>0.87**</i>	<i>0.92**</i>	<i>0.79**</i>

Levels of significance: *0.05, **0.01 (two-tailed); the coefficient is indicated in italics if $p \geq 0.6$

values > 6.5 (industrial areas, city squares, and to a minor account residential areas). We think that this observation could be explained by the enhanced mobility of Sb(V) in neutral to alkaline environments (Cai et al. 2015), which favors leaching to the subsoil.

Irrespective of the UST, there are high to very high correlation coefficients of Sb with the typical urban HM representatives Pb, Cu, Ni, and Zn. The high correlation coefficient very likely reflects the intensive use of Sb and these elements in industrial products and non-ferrous metallurgic processes (alloying, smelting) (Birke et al. 2011). In substantially modified soils, the high correlation coefficients are very likely caused by the anthropogenic deposition of rubble and debris that can contain many residuals of these industrial processes. Since these elements are also emitted to the atmosphere, the peri-urban area of the BMA is also affected by airborne pollution, resulting in high Spearman rank correlation coefficients even in forest and agricultural soils. The moderate to high correlation coefficient with Fe in forest soils, usually Podzolic

Cambisols (Senate Department for Urban Development and Housing Berlin 2018), is very likely due to the sorption of Sb(III) and Sb(V) to goethite (Leuz et al. 2006).

3.6 Single Pollution Index and contamination factor

Single Pollution Index (PI) is one of the most accurate indices when pollution by a single element should be assessed (Kowalska et al. 2018). The PI was determined for 901 topsoil samples, using LGB and RGB of topsoil horizons (A horizons). Depending on the selection of the geochemical background value, the calculation of PI and subsequent classification into PI classes produces different outcomes (Online Resource 8a + b). The utilization of RGB unfolds a very high (28.6%) or high (25.1%) Sb pollution rate (Table 4) so that more than 50% of the topsoils are rated as strongly polluted. The share of very high and high polluted topsoils diminishes when LGB is used. In this case, 11.5 and 9.3% of the samples are very high or high polluted, while 26.6% are considered unpolluted.

Table 4 Percentage share of topsoil samples in the respective PI class (N = 901), modified acc. to Kowalska et al. (2018) and respective C_f class (N = 901), division of classes acc. to Håkanson (1980)

PI class	PI value	Soil pollution	Reference value (LGB) [%]	Reference value (RGB) [%]
1	PI < 1	Absent	26.6	8.7
2	PI ≥ 1 and < 2	Low	35.1	17.5
3	PI ≥ 2 and < 3	Moderate	17.4	20.1
4	PI ≥ 3 and < 5	Strong	9.3	25.1
5	PI > 5	Very strong	11.5	28.6
C _f class	C _f value	Contamination	Baseline value (BV) [%]	
1	C _f < 1	Low	2.3 ^a	
2	C _f ≥ 1 and < 3	Moderate	2.1	
3	C _f ≥ 3 and < 6	Considerable	9.8	
4	C _f ≥ 6	Very high	85.8	

^a Values below LOD, that have been intentionally set to zero

Depending on the selected background value, topsoil samples in the BMA are, on average, low (LGB) ($\text{median}_{\text{PI}}$: 1.58) or strongly (RGB) ($\text{median}_{\text{PI}}$: 3.20) polluted with Sb. RGB pollution index of single samples for Sb ranges from 0.39 to 577.79 (Table 5), where the high PI_{RGB} values (>30) could be found regularly in a public park on Eiswerder Island. Other single sites, highly polluted with Sb, are located on the Berlin Wall border strip ($\text{PI}_{\text{RGB}} = 74.74$), and on a former shooting range site ($\text{PI}_{\text{RGB}} = 183.5$). Within the respective USTs, some single samples occur where the origin of Sb pollution could not be specified and is assumed to be related to technogenic material. Median PI values for Sb decrease in the following order:

(mixed areas \gg) roadside soils $>$ industrial areas $>$ city squares $>$ allotment gardens $>$ parks and urban green spaces $>$ residential areas $>$ public service and other special uses $>$ agricultural areas $>$ fallow areas $>$ forests.

Like PI, C_f was determined for 901 topsoil samples to show the contamination with Sb in comparison to BV (Online Resource 9). As the pre-industrial BV is used as a reference value for the calculation of contamination levels, all samples with an Sb content $>$ LOD are considered at least as moderately contaminated. 85.8% of the samples count as very high contaminated, with a maximum C_f value of 2476 times the BV. 9.8% of the topsoils are contaminated considerably, and just 2.1% (or 19 samples) are considered moderately contaminated (Table 4).

Determining pollution indices in urban environments can be a challenging task that could cause false assumptions. Generally, the geochemical background values can vary considerably from region to region. Depending on the selection of the background (local or regional), our assessed values and consequently, the degree of soil pollution or contamination for topsoil samples in BMA differ significantly (Online Resources 8 and 9). At first glance, the utilization of a site-specific local background value (LGB) might seem promising for giving better results than the regional background (RGB). In industrialized countries, such as Germany or Poland, however, the calculation of pollution indices can easily lead to misinterpretations, if the background value itself is affected by man-induced geochemical alterations. By the comparison of the RGB to the BV of the C horizon, we

can also note an approximately four-fold Sb enrichment. As Reimann and Garrett (2005) already mentioned, it is self-evident that, in this context, the ratio between topsoil (A horizons) and subsoil or parent material (B or C horizons) is not exclusively the result of anthropogenic contamination, but also due to natural soil formation processes (e.g., Mazurek et al. 2017, 2019). Therefore, we believe that the C_f , which uses the average background values from the upper continental crust (e.g., Turekian and Wedepohl 1961; Kabata-Pendias 2011) or BVs, is not appropriate to assess soil pollution in the topsoil. Instead, RGBs from uncontaminated rural sites and the occurring lithological units should be used.

However, our results prove that PI can be a useful and easily accessible tool to assess and map the enrichment of Sb and other HMs in topsoils as well as its distribution in natural and urban areas. Nonetheless, it should be highlighted that the selection of the background value (for PI and C_f) is essential. Particularly for soil protection issues or a risk assessment, the raw values provide more meaningful information than pollution indices alone. For an evaluation of these data, guideline values for Sb based on soil texture, mobility, speciation, and soil parameters have to be determined.

3.7 Modified degree of contamination

mC_d is a complex pollution index that summarizes the contamination factors of all analyzed HMs (As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Zn) for each sample to determine the overall degree of contamination. By assessing the mC_d , we computed how much of the soil contamination in the respective USTs can be attributed to Sb (Table 6). To calculate the mC_d , we used the modified Håkanson (1980) equation by Abraham and Parker (2008) and evaluated the mC_d values with respect to LGB and RGB (Online Resource 10a + b). This index was evaluated exclusively for complete observations ($N = 869$), including the single values $<$ LOD. The main advantage of the mC_d , compared to the original Håkanson eq. (Håkanson 1980), is that it is not limited to eight pollutants and can include any number of analyzed elements. Additional classes

Table 5 Maximum, average, and minimum PI values ($N = 901$), grouped by urban structure type and respective background value (RGB and LGB), maximum (max), and minimum (min) values are just given for RGB; abbreviations for USTs, see Table 2

UST	Total	Res	Mix	Ind	Pub	Fal	Rss	For	Agr	Prk	Csq	Alg
Max RGB	577.79	15.10	267.74	577.79	94.90	74.74	37.29	183.49	74.74	75.69	30.74	31.36
Med LGB	1.58	1.46	10.51	2.47	1.39	1.08	2.94	0.87	1.22	1.85	2.26	1.95
Mean LGB	3.45	1.61	23.27	13.10	4.14	2.06	3.94	2.34	3.34	2.59	3.12	2.62
Med RGB	3.20	2.96	21.35	5.01	2.82	2.19	5.97	1.77	2.47	3.77	4.58	3.97
Mean RGB	7.01	3.28	47.25	26.60	8.41	4.18	7.99	4.74	6.78	5.26	6.33	5.33
Min RGB	0 ^a	0.47	2.39	0.51	0 ^a	0 ^a	0.70	0 ^a	0 ^a	0 ^a	2.26	0.39

^a Values below LOD, that have been intentionally set to zero

Table 6 Median pollution indices (PI_{RGB}) for single elements, averaged overall degree of contamination (mC_d) of these pollutants in the BMA ($N=869$) and the percentage share of contamination that can be attributed to Sb, grouped by UST, reference value: RGB, division of classes acc. to Abraham and Parker (2008)

UST	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	Zn	mC_d	Sb / $\sum PI_9$ [%]
Res	1.23	7.15	4.40	3.14	9.48	3.31	2.77	2.96	8.18	5.32	6.94
Ind	1.49	9.25	4.60	2.94	15.79	4.06	3.40	5.01	12.31	6.84	8.51
Pub	1.50	8.51	5.06	2.89	9.89	3.53	2.27	2.82	8.41	5.19	6.28
Fal	1.11	4.85	4.22	2.67	7.19	3.50	1.87	2.31	5.98	3.94	6.85
Rss	1.31	9.95	4.41	3.23	19.88	3.97	4.22	5.97	11.93	7.11	9.20
For	1.21	0.78	1.83	1.16	2.27	1.35	1.51	1.72	1.54	1.68	12.88
Agr	0.98	3.19	3.65	2.42	5.61	2.33	1.29	2.39	3.29	2.83	9.49
Prk	1.57	7.08	4.69	2.82	12.33	3.74	3.64	3.77	9.65	5.83	7.64
Csq	1.63	8.13	4.78	3.31	15.40	3.89	4.60	4.58	13.30	6.95	7.69
Alg	1.39	9.13	4.37	2.95	17.86	3.54	4.00	4.02	16.47	6.95	6.30
Total	1.36	6.36	4.21	2.69	10.09	3.39	2.90	3.27	7.90	5.04	7.75

have been defined by Abraham and Parker (2008) to evaluate the overall degree of soil contamination more accurately. Calculation of mC_d revealed that, in total, roadside soil is the most contaminated UST of the BMA, succeeded by promenades and city squares, allotment gardens, and industrial zones. Near-natural soils in forests, agricultural areas, and fallow areas, in contrast, are the weakest polluted USTs. On average, the former USTs are classified as highly polluted ($mC_d: \geq 4-8$), whereas the latter USTs are rated as low to moderately polluted ($mC_d: \geq 1.5-4$). Uncontaminated or very low contaminated topsoils ($mC_d: < 1.5$) are occurring in the most pristine forest areas, only, while very high to extremely high contaminated topsoils are also present in the peri-urban parts of the BMA (Online Resources 10a + b). By determining the mC_d , we also obtained that Sb accounts for a large share of overall contamination in the BMA (median: 7.75%). Due to its relatively high accumulation compared to the RGB, Sb contributes significantly (~9.5–13%) to the total overall degree of contamination, especially in peri-urban soils (forests and farmland) (Table 6). Since Sb is at a contamination level like the main pollutants (Cu, Pb, Zn), it can be considered a key pollutant, at least in some USTs of the BMA (Online Resource 11). As an effect of more elements included in this index, the distinct distributional pattern of Sb in the city center disappears, and high contamination values are not limited to the inner-city area anymore. Very high mC_d values can also be caused by contamination with other HMs.

4 Conclusions

Due to the long-lasting history of emissions from industry, traffic, and coal combustion, topsoils of the Berlin Metropolitan Area are highly polluted with Sb and other heavy metals. Our case study revealed that Sb is a primary pollutant in the BMA, which has been neglected in most of the previous urban geochemical studies so far, although its

occurrence and enrichment is specific for urban soils. The distribution of Sb in the BMA can be directly attributed to diffuse, point, and linear anthropogenic sources. By our research, we demonstrated that the spatial distributional pattern of Sb in the Berlin Metropolitan Area is primarily related to vehicular emissions, historical, and recent land-use, and the existence of technogenic parent material. An elevated Sb content was predominantly measured in the Wilhelminian Belt, which has a long history of urban-industrial land-use. In this context, the pseudo-total Sb content and its distribution is reflecting the overall degree of early twentieth century's industrialization and urbanization. Generally, the Sb content tends to decrease from the city center to the suburbs. Especially, anthropogenically altered or technogenic soils of the Berlin Metropolitan Area can be severely contaminated with Sb and other heavy metals. Technogenic material is not always restricted to the topsoil, though. Further studies on metropolitan soils should be carried out to examine if leaching of Sb to the subsoil already caused an enrichment. However, the Sb content in the urban area is also influenced by numerous local site conditions and the distance from point or linear emission sources (traffic, industry). Our research in several study areas showed that due to hedges and other local barriers, the Sb content may decrease rapidly within the first 100 m from roadsides, for example. One major disadvantage in our study was the accessibility of residential and other private properties that resulted in few sampling sites in comparison with public areas such as parks and forests.

Studies on antimony in urban environments are still restricted to areas of a limited extent only. Thus, we suggest that geochemical studies in other metropolises worldwide should be carried out to investigate whether our findings can be transferred to other metropolitan regions with similar and different natural conditions, development and history. The calculated pollution indices indicate an anthropogenic accumulation of Sb in topsoils of the BMA. However, the determination of pollution indices in urban areas may be subject to errors.

Especially, the arbitrarily defined scales of the individual indices to prove soil pollution or enrichment should be viewed critically. The environmental risk assessment in metropolitan areas should therefore rather be based on threshold and guideline values as a function of UST and site-specific soil parameters instead of pollution indices. For ecological and environmental issues (e.g., risk assessment), we believe it is essential to conduct large-scale geochemical surveys on heavily contaminated (urban) land-use types such as sewage farms, industrial areas, and shooting ranges. Further sampling campaigns in potentially highly polluted areas are already set up and will provide new insights on the fate of antimony in the urban environment of the Berlin Metropolitan Area.

Acknowledgments The authors would like to express their special thanks to Anja Körle (HU Berlin) for assistance in the laboratory and the Senate Department for the Environment, Transport and Climate Protection Berlin (SenUVK), student co-workers and local partners without whose agreement a sampling of this extent in the BMA would not have been possible.

Funding Information Open Access funding provided by Projekt DEAL.

Compliance with ethical standards

Conflict of interest Kolja Thestorf (corresponding author) has received a travel grant for attending the SUITMA 10 conference from the German Academic Exchange Service (DAAD Kongressreisen, Grant No. 57445178). Mohsen Makki declares that he has no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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