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SOILS AND SEDIMENTS IN URBAN AND MINING AREAS

Heavy metals and benzo[a]pyrene in soils from construction and demolition rubble

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Abstract

Purpose Rubble is an important component of urban soils worldwide, especially in Europe. In Berlin, Germany, rubble-composed soils cover about 17 % of the total city area and 60 % of the inner city. This study assesses the contamination status of rubble soil, particularly for heavy metals and benzo[a]pyrene (B[a]P).

Methods The results of 164 soil surveys in Berlin, including more than 2,000 analyzed soil samples of topsoils, rubble subsoils, and natural material, have been analyzed for typical contamination patterns.

Results The concentrations of all contaminants range over several orders of magnitude and follow negatively skewed log-normal distribution functions. For rubble-containing subsoils, proportions of 34, 71, 67, 68, 74, and 61 % of the analyzed samples exceed precautionary values of the German Soil Conservation Act, regarding Cd, Pb, Cu, Zn, Hg, and B[a]P, respectively. Similar results were found for topsoils. A minor part of the soils is contaminated with Cd, while Pb and Hg are the most typical contaminants of rubble material. In contrast to topsoils and rubble-containing subsoils, the majority of the natural subsoil material is not contaminated. Only low to moderate positive correlations were found between the contaminants.

Conclusions Compared to natural soil material, rubble-containing soil materials show clearly elevated concentrations of heavy metals and B[a]P. As the most characteristic contaminants for rubble are Pb and Hg, these heavy metals should first be analyzed as proxy contaminants.

Keywords Urban soil · Construction and demolition rubble · Heavy metals · Benzo[a]pyrene · Technosols · Geochemical load index

1 Introduction

Construction and demolition rubble is one of the most common anthropogenic materials in urban soils (Bridges 1991; Meuser 2010). Rubble-composed soils, classified as Urbic Technosols according to the FAO-WRB classification system (IUSS Working Group 2006; Rossiter 2007), prevalently contain technogenic artifacts like bricks, mortar, and concrete (e.g., Blume and Runge 1978; Short et al. 1986; Wessolek et al. 2011). Construction and demolition rubble also contains ash, rubble from infrastructure (asphalt, ballast), slag, chars, wood, and glass (Blume and Runge 1978; Hiller and Meuser 1998a). Disposed rubble material is often polluted and contaminates Technosols (e.g., Short et al. 1986; Burghardt 1994; Gras et al. 2000; Shaw et al. 2010). Technogenic components frequently exhibit extremely high heavy metal concentrations. Particularly for slags and ashes, high concentrations are reported (Blume and Hellriegel 1981; Meuser and Blume 2001; Cloquet et al. 2006). Furthermore, the concentrations of PAHs can be elevated if, e.g., tar-based rubble from infrastructure or tar paper is deposited (Meuser 1996b). Raised PAH concentrations also are related to fire-affected rubble (Smettan and Mekiffer 1996). Besides the disposed technogenic material itself, the proximity to industrial facilities and trafficways leads to elevated levels of contaminants of Technosols and natural soils in the urban areas (e.g., Manta et al. 2002; Morton-Bermea et al. 2002; El Khalil et al. 2013).

Especially in Germany, Urbic Technosols are widespread due to bombing raids in the end of World War II and the interrelated emergence of a huge amount of rubble (Burghardt 1994). Meuser (1996b), for instance, found anthropogenic

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artifacts, particularly construction and demolition rubble, in 56.3 % of analyzed soil profiles in the city of Essen, Germany. At sports grounds, parks, and allotment gardens, the ratio of rubble-containing soils can even be higher (Hiller and Meuser 1998b). Kneib and Braskamp (1990) reported up to 74.6 % of tipped soils to be frequently containing rubble (Wolff 1996) in the inner city of Hamburg, Germany.

The German Soil Conservation Act (Bundes Bodenschutzgesetz 1998) defines waste and rubble disposal areas as suspected sites of harmful soil changes, assuming contamination due to the deposition of technogenic material. For risk assessment and further rehabilitation measures of those sites, soil surveys are frequently conducted.

Research on urban soil quality mainly concentrates on properties of the topsoil. For instance, topsoils of Berlin are already investigated and documented in detail so far (Fellmer et al. 1993; Birke and Rauch 1997; Birke and Rauch 2000). In contrast, there is still a lack of information for subsoils. In this study, we analyze, summarize, and discuss the heavy metal and benzo[a]pyrene contamination patterns of a very large number of rubble-containing soils, topsoils, and natural subsoils in the urban area of Berlin. We identify characteristic contaminations, calculate their probabilities, discuss contamination pathways, and suggest proxy indicators for a faster and cheaper soil contamination assessment, based on the statistical certainty provided by the large number of analyzed soil samples.

2 Material and methods

2.1 Study area

The geomorphology of Berlin is dominated by a glacial valley in the inner city and moraine plateaus in the north and in the south, which were formed by the Weichselian glaciation. The natural substrates in the inner city are mostly alluvial sands, while soils on the plateaus developed from marl and loamy sands.

Construction and demolition debris have always been dumped on-site during the city's 775-year-long history. However, the rubble depositions after World War II dominate in the soils in terms of covered surface area. In 1945, Berlin's built-up area was approximately 72 km^2, with 28.5 km^2 of it affected by bombing raids (Vertriebene and Kriegsgeschädigte 1967). At the end of the war, 19.5 % of the buildings were completely or irreparably destroyed (Statistisches Landesamt 1963; see also Fig. 1). The amount of material from rubble clearance is reported to range from 55 to 100 Mio. m^3 (Fichtner 1977). The major part of it was tipped into landfills (Keiderling 1999), and the minor part was deposited throughout the city at non-built-up areas, into bomb craters, parks, and backyards. Today, rubble landfills make up an area of 8.7 km^2. During construction activities in the younger history, rubble was continuously deposited in the inner city until the early 1970s. As a consequence, in the densely populated inner city, undisturbed naturally layered soils rarely exist. So, today, the area covered with rubble soils (blackish area in Fig. 2) or soils partly mixed with rubble (grayish area in Fig. 2) is about 133 km^2, which is 7 % of the whole administrative area and almost 60 % of the inner city. A typical profile of a building rubble-composed soil is shown in Fig. 1.

2.2 Database

Two thousand four hundred eighty-six soil data sets from 164 soil surveys from six of the 12 district agencies of Berlin were analyzed. The surveys were carried out due to the fact that technogenic materials have been found, which according to the German Soil Protection Act, implies the suspicion of harmful soil changes. Additionally, several surveys were conducted as part of building and excavation operations. At the respective sites, the contamination status was analyzed in order to decide on further soil material management like excavation, remediation, etc. The database comprises all types of soils and land use.

The soil sampling was predominantly carried out by soil core drilling, and only some soil pits were established. On average, each survey is based on ten soil core drilling points or soil pits with three sampling depths. Sampling depths did not necessarily correspond to soil horizons, and samples or mixed samples were taken in steps from 0–0.3 m, 0.3–1 m, 1–2 m, 2–3 m, etc. Most of the surveyors started sampling at 0.3–1 m and ended at 4 m depth, and the maximum sampling depth was 10 m. In several surveys, the sampling depth of the natural material started only at 3 m since it was covered with construction and demolition debris. The number of topsoil samples is smaller ($n=77$).

From the surveys, we can distinguish between the following three substrate classes: material from the topsoil layer (TSM), material from rubble-containing layers (CDM), and subsoils composed of natural soil material only (NSM). The TSM was mainly sampled from 0 to 0.3 m. The topsoils either have developed by pedogenesis or were applied as artificial layers. Some topsoils were anthropogenically changed, e.g., by addition and mixing of materials such as compost or sand. The CDM contains appreciable amounts of rubble, with unclear origin. It can include old building remnants, rubble from World War II, as well as younger construction and demolition debris. In approximately 90 % of the surveys, the layers deeper than 0.3 m were completely filled up with anthropogenic material. This also includes strongly anthropogenically influenced natural materials as, e.g., crushed stones used as construction material or sand which was used as building additive in mortars. The NSM includes all natural layered subsoils or relocated natural soil materials, free of any notable rubble. The predominant natural substrates documented in the surveys are sands. Other substrates, e.g.,

Fig. 1 *Left* situation in Berlin, Germany, 1945 (photo: Bundesarchiv, Bild 183-J31345/CC-BY-SA 3.0, with permission). *Right* typical Urbic Technosols in the inner city of Berlin, Germany (photo: B. Kluge, TU Berlin)

developed from marl and loam, are not considered as individual substrate classes in the following, since their fraction is less than 5 % of the examined soil samples ($n=21$ and $n=6$, respectively).

2.3 Methods

All TSM, NSM, and CDM samples were analyzed without any spatial reference due to privacy protection. The data sets can

Fig. 2 Distribution of rubble-containing soils in Berlin, Germany, for the whole city and for the inner city, encircled by the city train ring. *Grayish areas* demark soils partly filled up with rubble, while *blackish areas* demark soils predominantly filled up with rubble. Modified map from Umweltatlas Berlin (2008)

belong to the same or different sites; thus, sample numbers of the three substrates are not equal. In the evaluation, we did not distinguish between different sampling depths for CDMs and NSMs. We only included data of surveys, in which soil substrates and technogenic components are explicitly listed. The ratio and the composition of the single anthropogenic components were mostly estimated by visual criteria (Table 1). Second, only data sets were included, for which chemical analyses complied with ISO standards. The respective analytical methods are given in Table 2. The heavy metals and benzo[a]pyrene (B[a]P) are discussed in terms of total amounts.

The statistical analyses of the data set included the distribution function of the mentioned chemical parameters. The correlations between single contaminants were determined using Spearman's rank correlation coefficient (Spearman 1910), whereby concentrations smaller than the detection limits have been excluded from correlation analysis. The distributions of the concentrations and correlations of the contaminants Cd, Pb, Cu, Hg, Zn, and B[a]P were analyzed for CDM and NSM only, since the number of topsoil data is insufficient. The significance of the contamination differences for the three substrate classes was tested using the Kruskal-Wallis test for $p=0.05$ (Kruskal and Wallis 1952). The same statistical test was applied to evaluate whether the most common technogenic components as bricks, mortar, slag, and ashes in the CDM samples differ significantly from those CDMs without these respective components. For the estimation of soil contamination by heavy metals and B[a]P according to the geochemical background, we used the geochemical load index GLI_i; (Müller 1979) which is defined by

$$\mathrm{GLI}_i = \log_2 \frac{C_i}{B \cdot 1.5} \qquad (1)$$

Table 1 Fractions of technogenic components and natural material in construction and demolition debris layers from soils in Berlin, Germany (sites, $n=164$; soil samples, $n=1{,}771$)

Component	Fraction [% (*v*/*v*)]	Number
Bricks	0–70	1,625
Slag	0–60	562
Mortar	0–50	714
Ashes	0–50	88
Ballast	0–50	42
Concrete	0–20	251
Charcoal	0–20	50
Tar	0–15	25
Glass	0–10	231
Wood	0–10	52
Soot	0–2	13
Natural material	0–86	95

Table 2 Analytical methods (ISO) and their detection limits (DLs) for the chemical parameters as applied in the soil surveys

Parameter	Methods	DL (mg kg^{-1})
EC	ISO 11265	–
pH	ISO 10390	–
Pb	ISO 11047	0.03
Hg	ISO 16772	0.006
Ni	ISO 11047	0.01
As	ISO 11047	0.02
Cr	ISO 11047	0.03
Cd	ISO 11047	0.01
Cu	ISO 11047	0.007
Zn	ISO 11047	0.01
B[a]P	ISO 13877 or Soxhlet extraction	0.001

where C_i is the concentration of an element in the soil (mg kg^{-1}) and B is its background concentration in the corresponding region or country. For C_i, we applied the median of the corresponding contaminant distribution, in order to characterize a distribution instead of a single value. The background concentrations for subsoils in Germany are given for different texture classes by LABO (2003). Since sandy soils are predominant in the evaluated soil surveys (>95 %), the concentrations for sandy soils were applied. These background values represent the 90 % quartile of subsoils from up to 608 analyzed soil profiles without any regionalization and are reported for the discussed contaminants except for As and B[a]P. Thus, for As and B[a]P, background values for topsoils under agricultural use were applied. The contamination classes according to the GLI are given in Table 3. GLI values smaller than 0 indicate a non-polluted or even a depleted soil.

3 Results and discussion

3.1 Soil reaction and electrical conductivity

The pH values follow a normal distribution function. The pH values range from 6.2 to 9.3 for TSMs, from 3.5 to 12.6 for

Table 3 Classification of contamination according to the GLI_i (Müller 1979)

GLI_i	Level of contamination
<0	Depleted to non-polluted
0–1	Non-polluted to slightly polluted
1–2	Slightly to moderately polluted
2–3	Moderately polluted
3–4	Moderately to highly polluted
4–5	Highly polluted
>5	Very highly polluted

CDMs, and from 4.4 to 13.0 for NSMs (Table 4). A portion of 91 % of the CDMs and 84 % of the NSMs are at least slightly alkaline. According to Gerstenberg and Smettan (2005), the pH of natural top- and subsoils in the area of Berlin ranges from slightly to strongly acidic. This, however, cannot be the case for subsoils of the northern moraine plateaus as these developed from marl (lime and loam). Therefore, we interpret most of the pH in the slightly alkaline and alkaline range of NSM as geogenic or as the result of secondary liming due to carbonate-rich ground- and seepage waters (cf. Jim 1998). Apart from the NSMs, the analyzed soils exhibit elevated pH values, which indicate a strong anthropogenic impact. The alkaline soil reaction of the TSM might be the result of deposition of alkaline urban dust (cf. Anttila 1990) or mixing with underlying CDM. The alkaline characteristics of the CDMs can be mainly attributed to carbonate-rich components such as mortar, slags, and ashes (Meuser 1993; Burghardt 1994; Bridges 1991). Schleuß et al. (1998) reported a ratio of carbonates in Urbic Technosols of up to 14 % (*w*/*w*). The high amount of carbonates in CDMs constitute a long time buffer capacity, which persists over several hundreds of years (Hiller 1996) and which will decrease the bioavailability of heavy metals (e.g., Chuan et al. 1996; Ge et al. 2000).

The electrical conductivity (EC) follows a negatively skewed log-normal distribution function for CDMs and NSMs. The CDMs and the NSMs show extreme values of up to 9,292 and 8,020 μS cm^{-1}, respectively (Table 4). High values can be attributed to the presence of ashes in the soil (cf. Nagamori et al. 2007) or due to other anthropogenic inputs, such as fertilizers or deicing salts (cf. Helmreich et al. 2010).

Table 4 General properties, statistical parameters of contaminant concentrations, and GLI$_i$ index

	pH	EC (μS cm^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	B[a]P (μg kg^{-1})	Ni (mg kg^{-1})	Cr (mg kg^{-1})	Hg (mg kg^{-1})	As (mg kg^{-1})
Background value	–	–	0.24	12	7	24	46^{a}	9.4	15	0.05	4.0^{a}
Precautionary value	–	–	0.40	40	20	60	300^{b}	15.0	30	0.10	25^{c}
TSM											
n	53	30	71	72	44	22	33	62	67	32	61
Arithmetic mean	7.5	287	0.66	103.1	46.3	101.5	440	12.2	23	0.31	5.2
Median	7.3	300	0.34	55.2	28.7	87.0	289	10.3	14	0.24	4.1
75 % percentile	8.2	398	0.97	81.0	40.5	117.5	613	15.9	26	0.41	7.1
90 % percentile	8.4	431	1.90	188.4	59.7	186.8	1,036	20.9	34	0.83	11.0
Max.	9.3	742	4.10	1,080	527.5	449.0	2,100	38.4	297	1.01	33.1
GLI$_i$ (median)	–	–	<0	1.6	1.5	1.3	2.1	<0	<0	1.6	<0
NSM											
n	693	350	735	773	631	471	639	617	719	708	743
Arithmetic mean	7.9	209	0.36	46.7	18.1	60.0	738	4.4	10	0.23	4.6
Median	8.0	85	0.01	9.0	6.0	12.0	100	2.100	3	0.01	1.1
75 % percentile	8.4	180	0.30	46.0	22.4	0.23	230	6.7	9	0.21	2.8
90 % percentile	8.8	421	0.97	102.8	44.1	47.9	727	11.6	17	0.58	5.6
Max.	13.0	8,020	16.2	2,694	718	2,284	108,000	88.2	1,690	7.00	848
GLI$_i$ (median)	–	–	<0	<0	<0	<0	<0	<0	<0	<0	<0
CDM											
n	1,397	957	1,600	1,641	1,328	1,011	1,422	1,335	1,544	1,427	1,591
Arithmetic mean	8.1	392	0.65	219.5	119.0	282.2	2,668	14.9	15	1.56	6.7
Median	8.1	189	0.04	77.2	28.4	99.4	496	8.9	10	0.29	3.6
75 % percentile	8.5	404	0.67	169.0	65.0	223.0	1,549	14.00	17	0.65	6.2
90 % percentile	8.9	989	1.50	422.0	148.3	583.0	4,371	30.3	30	1.60	12.0
Max.	12.6	9,292	25.30	14,093	25,000	14,000	460,000	428	466	1,100	619
GLI$_i$ (median)	–	–	<0	2.1	1.4	1.5	2.8	<0	<0	2.0	<0

TSM topsoils, *NSM* natural soil material, *CDM* construction and demolition material-containing soil

[a] Background value B[a]P and As for topsoils under agricultural use; other background values for sandy subsoils (LABO 2003); precautionary value of the German Soil Protection Act for sandy soils

[b] Precautionary value for sandy soils with organic matter content <8 %

[c] Precautionary value for playgrounds

3.2 Cadmium

The Cd concentrations exhibit a negatively skewed log-normal distribution for the NSM and CDMs (Fig. 3). A ratio of 51, 40, and 27 % of TSMs, CDMs, and NSMs, respectively, are above background concentration (see Table 4). The precautionary value (0.40 mg kg^{-1}) is exceeded for 47 % of the TSMs, 34 % of the CDMs, and 21 % of the NSMs. As it can be expected, the examined NSMs show significantly lower Cd concentrations than CDMs (n=735; p<0.05). Between TSMs and the other two materials, no significant difference could be found, resulting from a high variability of TSMs. This finding also applies for the other contaminants. Within the CDM, the samples containing slag and ashes show higher medians (0.28 and 0.07 mg kg^{-1}) compared to those without the respective component (0.01 and 0.04 mg kg^{-1}, respectively). These differences are significant for slag- and ash-containing CDM. Nevertheless, significant correlations between fractions of technogenic materials and Cd concentrations could not be found. For brick and mortar, no effects on Cd contamination could be identified. The same applies for the other analyzed contaminants, and thus, it is not discussed in the following.

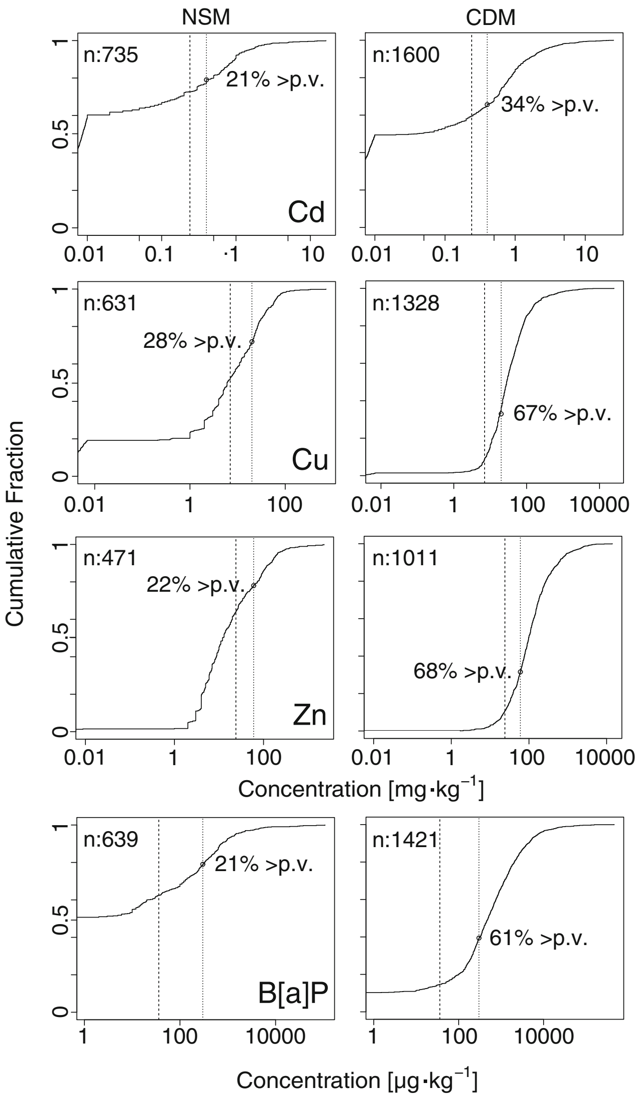

Fig. 3 Cumulative distribution of heavy metals and B[a]P. *Left* natural subsoil material (*NSM*). *Right* construction and demolition material-containing soil (*CDM*). *Roughly dotted lines* indicate background values; *finely dotted lines* indicate precautionary value (*p.v.*); *x*-axis starts with a value of detection limit

The results indicate that higher layers are more contaminated than deeper layers; thus, a contamination could have taken place from above after the materials have been deposited, e.g., from atmospheric deposition (Alloway and Steinnes 1999). The median Cd concentration is 0.34 mg kg^{-1} for TSMs, which is nearly identical to topsoil samples taken by Birke and Rauch (1994) as they found a median of 0.32 mg kg^{-1} for the densely populated residential areas in Berlin. The elevated concentrations in CDMs might be the result of secondary contamination but are partly a characteristic of the rubble itself. Cd contaminations can arise from cadmium-based paint (cf. Blume and Hellriegel 1981), existence of metal work slags (cf. Meuser and Blume 2001), or ashes. Ashes from coal combustion show concentrations of 10 to 60 mg kg^{-1} and have been indentified to contribute to the elevated Cd concentrations in the Berlin Urbic Technosols (Blume and Hellriegel 1981). According to the GLI_{Cd}, which is <0, none of the three substrate classes show a typical contamination with Cd (Table 4). For CDM, just in few cases, elevated concentrations were observed. Thus, building rubble is not a characteristic factor enriching Cd.

3.3 Lead

The Pb concentrations exhibit a negatively skewed log-normal distribution for the two considered substrates CDM and NSM (Fig. 4). The concentrations range over several orders of magnitudes up to 14,093.0 mg kg^{-1} for CDM. The background concentration of 12.0 mg kg^{-1} (LABO 2003) is exceeded by 91 % of the CDMs but also by 45 % of the NSMs. The majority of CDM (71 %) and TSM (68 %) have Pb concentrations higher than the precautionary value of 40 mg kg^{-1}. In contrast, only 27 % of the NSMs show concentrations higher than the precautionary value. Again, the contamination of CDMs and NSMs is significantly different (n=773; p<0.05). Birke and Rauch (2000) documented a median of 109.0 mg kg^{-1} Pb in Berlin topsoils, which is double of the median (55.2 mg kg^{-1}) for TSM in our database. As we have analyzed soils which have partly been disturbed and engineered and which probably have constructed topsoils from hopefully high-quality raw material, a low contamination status can be at least expected compared to old urban soils, which have been included in Birke and Rauch's study. In contrast, in old or especially exposed urban soils, Pb contamination might be linked to direct industrial contamination or atmospheric deposition from industry, vehicle emissions

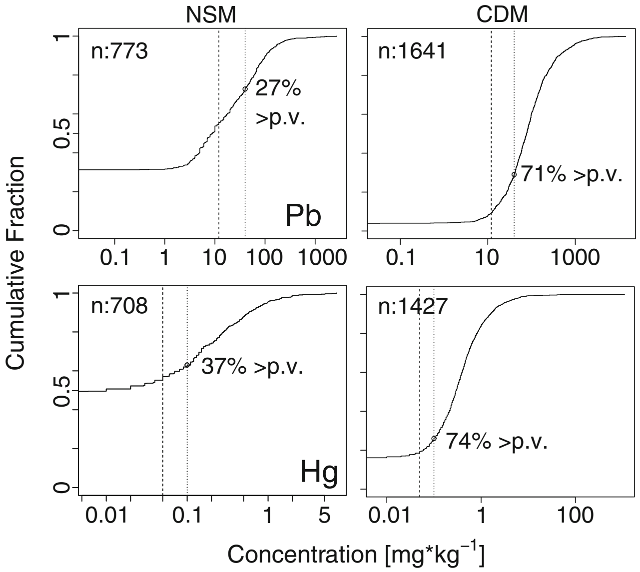

Fig. 4 Cumulative distribution of Pb and Hg. *Left* natural subsoil material (*NSM*). *Right* construction and demolition rubble-containing subsoil (*CDM*). *Roughly dotted lines* indicate background value; *finely dotted lines* indicate precautionary value; *x*-axis starts with a value of detection limit

(c.f. Galloway et al. 1967; Nriagu and Pacyna 1988; Blume and Hellriegel 1981), and street dust (c.f. Miguel et al. 1997). For CDMs, the mean concentration (219.5 mg kg^{-1}) is in a comparable magnitude as the mean of 395.0 mg kg^{-1} for subsoils reported by Smettan et al. (1993). The source of lead in CDMs containing soils can be linked to a variety of rubble-typical sources: lead-based paints (cf. Jacobs et al. 2002; Howard et al. 2013); lead lights and ceramic glaze (Blume and Hellriegel 1981); slag components, which can lead to concentrations higher than 10,000 mg kg^{-1} (cf. Cloquet et al. 2006); and ashes from coal combustion, with concentrations ranging from 1,000 to 20,000 mg kg^{-1} (Blume and Hellriegel 1981). The special contribution of slag and ash to the contamination can be confirmed by our results. As for Cd, slag- and ash-containing CDMs show significantly higher medians than CDMs without them (120.0/172.0 and 70.5/82.5 mg kg^{-1}, respectively). Further corroded or smelted water pipes (Smettan et al. 1993) or the deposition of lead batteries (cf. Pichtel et al. 2000) may contribute to elevated concentrations. Bricks and mortar, which are the most common component in the documented urban soils, show rather low to moderate lead concentrations of 14 to 103 and 310 mg kg^{-1}, respectively (Meuser 1996a; Nehls et al. 2013). The calculated GLI_{Pb} indicates that the majority of CDMs are moderately polluted (Table 4). The majority of NSMs feature no enrichment of Pb in comparison to the geogenic background concentrations ($GLI_{Pb}<0$).

3.4 Copper

The Cu concentrations follow a negatively skewed log-normal distribution for the NSMs and CDMs (Fig. 3). Ninety-one percent of the CDMs and 47 % of the NSMs show concentrations higher than the background value of 7 mg kg^{-1} (LABO 2003). The CDMs and TSMs show the highest concentration medians, and more than 67 % of them exceed the precautionary value of 20 mg kg^{-1}, but only 28 % of the NSMs. CDMs are significantly more contaminated with Cu than the NSMs (n=631; p<0.05). Again, slags and ashes could be identified as a crucial source of contamination. The CDMs containing these components show significantly higher medians (57.4 and 59.5 mg kg^{-1}) than those without (24.3 and 29.0 mg kg^{-1}, respectively). The copper concentrations with a median of 28.7 mg kg^{-1} of the topsoil samples are in a comparable magnitude as the results of the study of Birke and Rauch (2000), reporting a median of 37.0 mg kg^{-1}. Regarding CDM, several sources potentially induce elevated Cu concentrations: wood preservatives can lead to high concentrations (Bergbäck et al. 2001), and slag, a frequently found component in rubble, possesses elevated Cu concentrations (Meuser 1996a) as well as pipes, cables, and other electric installations. For the components, bricks and mortar (Blume and Runge 1978) were documented to have moderate Cu concentrations of 30 mg kg^{-1}. Besides the anthropogenic artifacts in the soil, atmospheric deposition and vehicle emission might particularly raise the Cu concentration of the topsoils (Nriagu and Pacyna 1988; Davis et al. 2001). On average, the CDMs show a slight to moderate pollution level (Table 4).

3.5 Zinc

The Zn concentrations for NSMs and CDMs exhibit a negatively skewed log-normal distribution (Fig. 3). The concentration of CDM ranges over several orders of magnitudes with a maximum of 14,000 mg kg^{-1}. The medians of the topsoil (87.0 mg kg^{-1}) and CDM (99.4 mg kg^{-1}) are approximately three and four times higher than the background value (24 mg kg^{-1}). The majority of analyzed TSMs and CDMs exceed the precautionary value. In contrast, the median of the NSMs is below the background and precautionary value. Meuser (1996a) reported even higher levels of Zn for soils filled up with rubble. He documented a mean of 610 mg kg^{-1}, which is more than two times higher than the mean of 282 mg kg^{-1} for the CDMs in this study. As for the other mentioned heavy metals, the NSMs have significantly lower Zn concentrations than the CDMs (n=471; p<0.05). Sources of zinc in the analyzed CDMs are presumably galvanized goods such as gutters, roof parts and kitchen tools, paints (cf. Bergbäck et al. 2001), slags (Shaw et al. 2010), ashes, and bricks in the rubble itself. Bricks show a moderate Zn concentration above the precautionary value. With 127 and 126 mg kg^{-1}, Meuser (1996a) and Shaw et al. (2010) mentioned quite similar results of Zn in bricks. Nehls et al. (2013) found concentrations ranging from 85 to 171 mg kg^{-1}. Our results could again identify a significant influence of slags and ashes, indicated by higher medians of those CDMs containing these components (176.0/262.5 mg kg^{-1} compared to 90.0/110.0 mg kg^{-1} for CDMs without slags and ashes, respectively). Since the database also includes industrial and traffic sites, emissions and tire and brake pad abrasions can be additional sources of zinc in the soil, particularly in the topsoil (cf. Davis et al. 2001; Councell et al. 2004). At least half of the topsoil and the CDM samples show a slight to moderate pollution according to the GLI$_{Zn}$ (Table 4). This indicates that CDM is responsible for an enrichment of Zn, since the majority of NSMs show no higher concentrations than the geogenic background.

3.6 Other heavy metals

As the heavy metals discussed above, concentrations of Ni, Cr, Hg, and As follow a negatively skewed log-normal distribution function for CDMs and NSMs. For both substrates, Ni, Cr, and As exhibit median concentrations below the precautionary value and even below the geological background value (Table 4). Thereby, the geological background of these trace metals (90 % percentile) for sandy subsoils is given by LABO (2003) without any regional or land use specification. The findings indicate that there is no relevant contamination linked with the deposition of rubble.

Hg concentrations show a different pattern. A portion of 37 and 74 % exceeds the precautionary value regarding NSMs and CDMs, respectively (Fig. 4). Also, TSMs show elevated concentrations of Hg with a median of 0.24 mg kg^{-1}. Again, the CDMs differ significantly from the NSMs, concerning all four heavy metals. As for the aforementioned metals, slag and ashes could be identified as components responsible for elevated Hg levels. The corresponding substrates with slag and ashes show significantly higher medians (0.41 and 0.39 mg kg^{-1}, respectively) than those without (0.24 mg kg^{-1} for both).

Birke and Rauch (2000), mentioning a median of 0.34 mg kg^{-1} in the high-density residential areas, ascribe the contamination to industrial land use, but they also found high concentrations in association with dumped rubble. The source of Hg in those rubble-composed soils might be attributed to mercury lamps or electrical inventory (cf. Rodrigues et al. 2006; Cheng and Hu 2011).

3.7 Benzo[a]pyrene

B[a]P is frequently used as a proxy substance for the contamination with PAHs as it is one of the most hazardous and carcinogenic of the PAHs (e.g., Collins et al. 1991). The concentrations of B[a]P can be described by a negatively skewed log-normal distribution (Fig. 3). The majority of the CDMs and TSMs exceed background (46 μg kg^{-1}) and precautionary (300 μg kg^{-1}) values. In contrast, only 21 % of the NSMs exceed the precautionary value. The concentrations of B[a]P in the NSMs are significantly lower than those of CDMs (n=639; p<0.05). Slag significantly contributes to soil pollution, as indicated by a higher median than that of CDMs without (910 and 360 μg kg^{-1}). For ashes, this could not be confirmed statistically. The high B[a]P contamination rate of CDM could be attributed to the presence of material from World War II. These materials frequently contain high amounts of ashes, slags, and incompletely burned, smoldered components (black carbon) (cf. Smettan and Mekiffer 1996; Gras et al. 2000). The fire spread during the bombing raids, and the related combustion of organic materials is the main source of B[a]P and other PAHs in rubble from World War II. Ruokojärvi et al. (2000) and Wobst et al. (1999) documented high PAH concentration in the soot and at surfaces of building inventories, respectively, after the fire. Tar-based components can also serve as sources of PAHs. Meuser (1996b) found total B[a]P concentrations of up to 148,000 μg kg^{-1} in such materials, which are frequently found in the CDMs and which can make up a ratio to 15 vol%, according to our database. Additionally, elevated levels of B[a]P and PAH can be attributed to recent atmospheric deposition (Baek et al. 1991). The concentration in TSMs might further be elevated due to urban dust inputs from traffic, which can exhibit concentrations of up to 2,200 μg kg^{-1} (Essumang et al. 2011). Overall, the majority of the TSMs show a moderate level, and the majority of CDMs show a moderate to high B[a]P pollution level, according to the GLI$_{B[a]P}$ (Table 4). It has to be considered that we applied the background concentration for topsoils under agricultural use for calculating the GLI$_{B[a]P}$. Subsoils can be expected to contain B[a]P at lower levels (e.g., Krauss et al. 2000). However, data for German subsoils are not available. This might have led to an underestimation of the GLI$_{B[a]P}$ and the fraction exceeding background concentration.

Table 5 Spearman's rank correlation coefficient between contaminants

	Cd	Cu	Zn	Hg	B[a]P
NSM					
Pb	0.36^{a}	0.55^{a}	0.56^{a}	0.62^{a}	0.60^{a}
Cd		0.40^{a}	0.46^{a}	0.25^{a}	0.32^{b}
Cu			0.84^{a}	0.53^{a}	0.57^{a}
Zn				0.63^{a}	0.58^{a}
Hg					0.32^{a}
CDM					
Pb	0.40^{a}	0.37^{a}	0.36^{a}	0.19^{a}	0.40^{a}
Cd		0.45^{a}	0.49^{a}	0.26^{a}	0.33^{a}
Cu			0.67^{a}	0.49^{a}	0.36^{a}
Zn				0.37^{a}	0.41^{a}
Hg					0.25^{a}

NSM natural soil material, *CDM* construction and demolition material-containing soil

[a] Highly significant (p<0.01)

[b] Statistically significant (p<0.05)

3.8 Correlations between the contaminants and identification of representatives

In general, we found low to moderate correlations between Cd, Pb, Cu, Hg, Zn, and B[a]P (Table 5). Between the pH and the contaminants, there is no meaningful correlation (coefficient <0.16). A strong correlation was found between Cu and Zn in NSMs. Besides, for Cd, the correlations between the contaminants are stronger for the NSMs as for the CDMs. This might be attributed to the higher heterogeneity of the CDM, with its various technogenic components in differing compositions.

Due to the low correlation between the contaminants, it is difficult to determine a single representative. Soil surveys, supporting decision making for further soil material management or remediation, should first test Pb and Hg concentrations, since these are the most characteristic ones for rubble. Additionally, Pb and Hg show the highest concentrations and impose a sufficient health risk to imply remediation measures. Other contaminants have to be additionally analyzed only if Pb or Hg concentrations are below the precautionary value.

4 Conclusion and outlook

Our study shows clearly elevated concentrations of heavy metals and B[a]P in rubble soils compared to the natural subsoil material. Thereby, the majority of these rubble soils are moderately to highly contaminated with Pb, Cu, Zn, Hg, and B[a]P, while Cd, Ni, As, and Cr are a minor concern. A high heterogeneity in composition and amounts of technogenic components leads to highly variable contaminant concentrations. Nevertheless, slag and ashes could be identified as crucial sources of elevated concentrations. The depth profiles of the contaminants' concentrations additionally suggest anthropogenic pollution after rubble materials were deposited. Pb and Hg are the most pronounced contaminants for rubble soils. We suggest analyzing them for a fast contamination assessment of the corresponding sites and further decision support for potentially required remediation. Only if Pb or Hg concentrations are below the precautionary value is an analysis of further contaminants necessary in order to assess the pollution status of the site and to decide whether remediation measures have to be conducted.

Although the area of Berlin is covered by contaminated Urbic Technosols to a large extent, groundwater monitoring does generally not show elevated heavy metal concentrations in the upper groundwater aquifer. However, recent studies have shown that rubble depositions pose a serious threat to the groundwater quality regarding sulfate.

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