

Contamination status and assessment of urban and non-urban soils in the region of Sulaimani City, Kurdistan, Iraq

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Received: 19 February 2016 / Accepted: 2 August 2016 / Published online: 16 August 2016
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Abstract Soil contamination, especially in urban areas, is a globally increasing threat. Yet, knowledge on the status of urban soils in recently and rapidly developing regions and semiarid areas is still scarce. In this study, soils were investigated from Sulaimani city that underwent rapid growth and urbanization in past decades. Properties and contamination of 91 topsoils from 11 areas of different anthropogenic impact were determined. Differences between urban and non-urban soils were attributed by principal component analysis to differences in contents of pedogenic oxides, carbonate, organic nitrogen and carbon, pH and CEC. Also total contents of potentially toxic elements (PTE) were higher; mean contents of Cd, Pb, Cu and Zn in urban soils were 0.35, 51.8, 78.6 and 163.0 mg kg⁻¹. The PTE contents increased with traffic volume and industrial emissions. The anthropogenic origin of contamination was further evidenced by significant enrichment of PTE in the top 0–5 cm compared to deeper topsoil layers. Additionally, mobility of PTEs was low in the clayey, alkaline soils. Contamination was substantially lower compared to many other cities, being explained by the short history of urban development in Sulaimani. Correspondingly, contents of polycyclic aromatic hydrocarbons were mostly not detectable. Contamination with PTEs was

assessed using pollution indices and classified as ‘moderate’ to ‘considerable’ in roadside soils and significant’ to ‘very high’ in soils from industrial areas, depending on the single element. Toxicity indices >0.5 revealed that adverse effects on ecosystem functions must be expected at several urban and especially industrial sites.

Keywords Urban soils · Potentially toxic elements · Depth distribution · Geoaccumulation indices · Contamination factors · Polycyclic aromatic hydrocarbons

Introduction

Urbanization, industrialization and automobile traffic are rapidly increasing in many areas of the world so that the related environmental contamination, occurring in closest proximity to humans, has often reached a disturbing magnitude that may pose a serious risk for urban residents and may adversely affect soil ecosystem services (Ajmone-Marsan and Biasioli 2010; Akoto et al. 2008; Luo et al. 2012). At the same time, urban soils can be used as an indicator of anthropogenic contamination (Wong et al. 2006). Hence, comprehensive investigations and assessments of urban soils are needed (Luo et al. 2012), but information is largely missing, especially in recently and rapidly developing regions and semiarid areas.

The city of Sulaimani is one of the largest cities of the Kurdistan Autonomous Region and the capital of the As-Sulaimani governorate. It is located in northeastern Iraq, on the edge of a wide mountain valley and has a semiarid, summer-dry climate. Due to a positive economic development, the population of the As-Sulaimani governorate increased from 1.36 million inhabitants in 1997 to 2.04 million in 2014 (Sulaimani Statistical Office 2014). This

Electronic supplementary material The online version of this article (doi:10.1007/s12665-016-5972-z) contains supplementary material, which is available to authorized users.

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was paralleled by a rapid urbanization and growth in industrial activities and traffic. The number of motor vehicles in Sulaimani city vastly increased from about 32,500 in 1999 to 425,800 in 2014 (Sulaimani Statistical Office 2014).

Typically, such urban development goes along with largely increasing gaseous and particulate emissions from industry, residential activities, waste management and traffic (Ahmed and Ishiga 2006; Amato et al. 2009; Imperato et al. 2003; Luo et al. 2012). Accordingly, air pollution and the deposition of dust and aerosols strongly incline (Trujillo-González et al. 2016), and existing reports on Sulaimani city also indicate increasing emission of dust and air pollution from traffic and industry, occasionally exceeding legislative limits (Sulaimani Environment Office 2009; Majid 2011).

Urban emissions are often a significant source of potentially toxic elements (PTEs) and organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) (Ajmone-Marsan and Biasioli 2010; Wei and Yang 2010; Wilcke et al. 1999b; Wong et al. 2006). The most abundant PTEs in urban soils that have been widely identified as anthropogenic pollutants are Pb, Cd, Cu, Zn, Hg, Cr, Co and Ni (Imperato et al. 2003; Luo et al. 2012; Trujillo-González et al. 2016; Wong et al. 2006). Of these, especially Pb, Cd, Cu and Zn originate from anthropogenic activities and are found widespread in urban soils (Cui et al. 2011; Peña-Fernández et al. 2015; Wei and Yang 2010) often at high contamination levels and exceeding precautionary values (Hu et al. 2013; Lee et al. 2006; Trujillo-González et al. 2016). The type and extent of soil contamination is frequently linked to the intensity of anthropogenic impact and varies, for example, between recreational, residential, traffic and industrial areas (Gu et al. 2016; Trujillo-González et al. 2016; Yan et al. 2015). Consequently, the determination and assessment of urban soil contamination in relation to anthropogenic activities is particularly important for the evaluation of environmental quality and protection (Akoto et al. 2008; Luo et al. 2012). For the assessment of soil contamination, several pollution indices have been suggested, e.g., enrichment factor (*EF*) (Buat-Menard and Chesselet 1979), geoaccumulation index (I_{geo}) (Müller 1969), contamination factor (*C_f*) (Håkanson 1980), pollution load index (*PLI*) (Tomlinson et al. 1980) and toxicity index (*TI*) (Azarbad et al. 2013).

Knowledge on the properties and contamination level of urban soils in the Kurdistan Autonomous Region is lacking, though. Even general soil information is primarily limited to the early work of Buringh (1960), giving an overview on the soil types of Iraq, and a few investigations on water and air contamination in Sulaimani city that also address soil physicochemical properties (Khorshid 1988; Majid 2011). Hence, the aim of this first comprehensive study was to identify and assess the contamination status of urban soils of

Sulaimani city. To this end, samples were investigated for Cd, Pb, Cu and Zn as representative indicators of PTE contamination and for PAHs as typical organic pollutants in urban soils. More detailed aims were (1) to identify the impact of human usage intensity by sampling sites of different exposition to traffic and industrial activities and (2) to determine the contamination status of urban soils compared to non-urban agricultural and pastoral land, whereby (3) it was hypothesized that the human impact also leads to changes in general soil properties. (4) Furthermore, it was aimed to differentiate between aboveground anthropogenic input of PTEs and belowground geogenic origin as well as to determine possible transport of PTEs within the soil by analyzing samples from three selected soil depths. Finally, (5) different pollution indices were tested for the comparative assessment of the contamination status of the different sites.

Materials and methods

Study area and soil sampling

Sulaimani city is located at 35° 33' N and 45° 26' E in the Zagros Mountains at an altitude of about 860 m above sea level (a.s.l.) (Figure 1). The climate is semiarid with 18.5 °C mean annual temperature and 600 mm mean annual precipitation and a dry season from June to October. The annual average wind direction is SW at a mean annual wind speed of 2.1 m s⁻¹ (Ahmed and Omer 2013). Plains south and west of the city are characterized by agricultural use and are surrounded by the Sagrama Mountains (911 m a.s.l.), while the mountains to the north and northeast, i.e., Piramagroon (3620 m a.s.l.), Azmar (1072 m a.s.l.) and Goyzha (1524 m a.s.l.), are directly adjacent to the city of Sulaimani. Mountain areas are characterized by extensively grazed grassland. Some of the rivers in the region are found in the Sulaimani area. In the west of Sulaimani flows the Qiliasan stream southward along the city, confluent with Kani-Ban stream to form the Tanjero River in the south of Sulaimani that is flowing eastwards (Fig. 1). Non-urban soils in the region of Sulaimani are classified as Rendzic Leptosols, Leptic and Vertic Kastanozems, Vertic Calcisols and Skeletic Fluvisols (FAO 2003). Soils are developed from underlying carbonate and mixed clastic and carbonate, forming the parent materials in the Sulaimani region (FAO 2003; Karim et al. 2008).

Soil samples were taken within the city of Sulaimani and in the surrounding areas in March–April of the years 2010 and 2011. In total, 91 sites were selected and allocated to 11 areas of different anthropogenic impact intensity (Table 1). This included 55 urban soils of Sulaimani city from parks, roads with low, semi-heavy and heavy

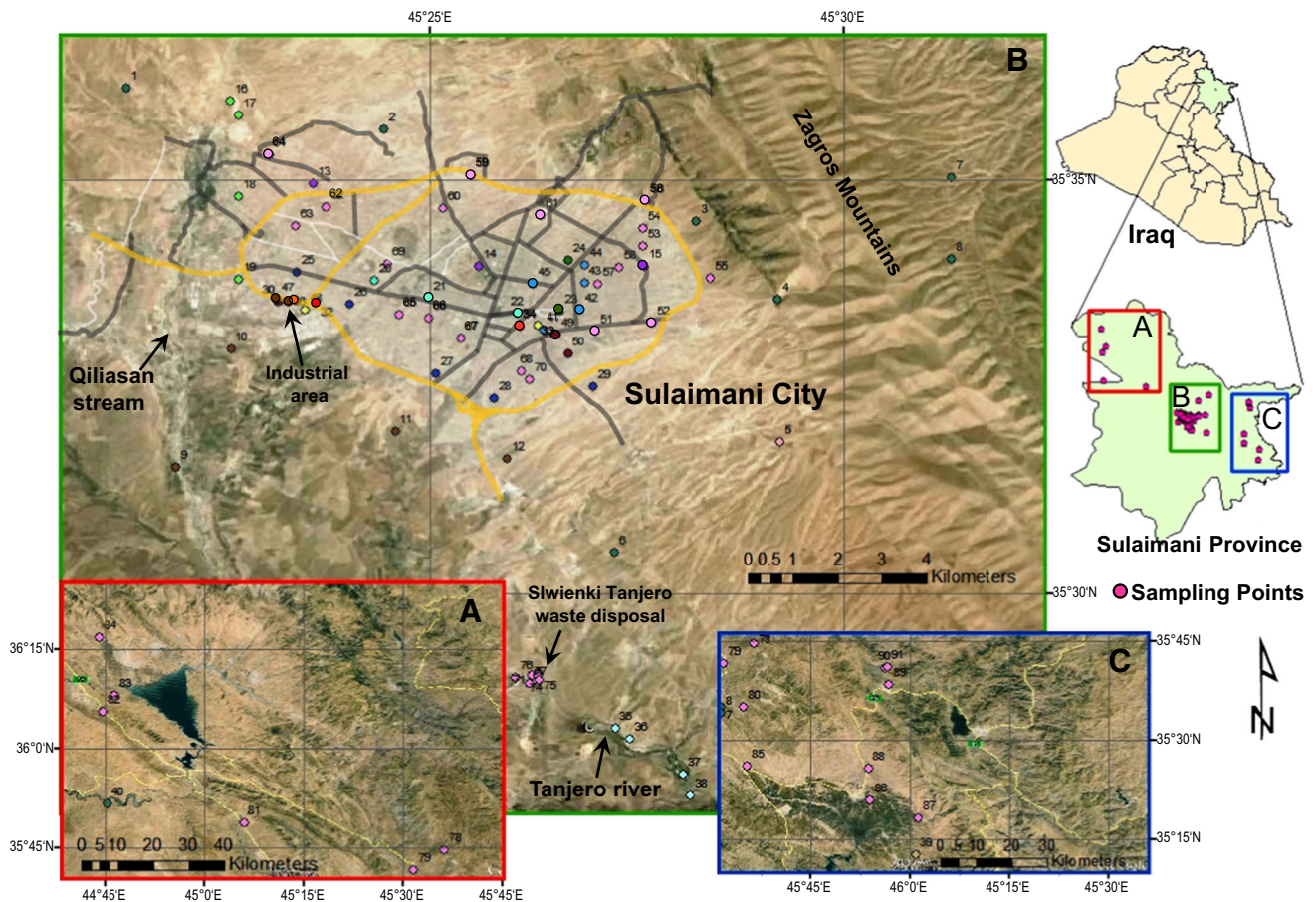


Fig. 1 Location of Sulaimani city within Kurdistan Autonomous Region, Iraq, with some of the major city roads highlighted, and soil sampling sites in areas of different anthropogenic impact (see Table 1) indicated by different colors. Satellite image from Google Earth

traffic, two industrial areas (comprising oil refineries, blacksmiths, car repair shops, automotive paint shops, car washes) and the waste disposal site Slwienki Tanjero that is located next to the Tanjero River. Samples were taken in different distances to the waste disposal site, increasing from 5 to 100 m. Additional four soils were sampled at the banks of the Tanjero downstream of the city. Two soils from war-affected areas were sampled at Halabja and Goptapa, about 70 km southeast and 130 km northwest of Sulaimani city, respectively. The sampling sites and areas of different anthropogenic impact intensity are listed in Table 1 and are shown in Fig. 1. For comparison, additional 30 sites of non-urban land use were sampled in the greater Sulaimani region, representing the remote mountainous area, alluvial soils from Qiliasan River upstream of the city and the most relevant agricultural areas in the entire province, i.e., Sharbazher, Dukan and Pishdar plains, Sharezoor plain and Penjwin.

Soil properties such as soil texture and major soil unit were determined in the field according to FAO guidelines for soil description (Jahn et al. 2006). Soil samples were collected from three replicate bores at each site, and

replicate samples were well mixed to reduce natural variations. Most soils were sampled at three different depths from topsoil horizons (0–5, 5–10, 20–30 cm; layer 1, 2 and 3, respectively), while mixed samples from the tillage horizon (0–30 cm) were taken from arable soils. Roadside soils were sampled within 1 m distance to the roadway, thereby ensuring that natural soil material and not technogenic material was sampled. Soil samples were air-dried, carefully ground with mortar and pestle, sieved to <2 mm and mixed prior to further analyses. For PAH analysis, samples were stored in acetone-washed, closed aluminum trays (Roth, Karlsruhe, Germany).

Laboratory soil analysis

Selected soil chemical properties were analyzed using standard procedures (Blume et al. 2011; USDA-NRCS 2004). The pH value was measured in a 1:2.5 soil/water suspension using a glass electrode (pH/Cond 340i plus, WTW, Weilheim, Germany); electric conductivity (EC) was determined in a 1:2 soil/water suspension with a TetraCon 325 conductivity cell (WTW, Weilheim, Germany).

Table 1 Sampling areas with different usage intensity and different probability of contamination in which the soils were grouped that were sampled at non-urban and urban sites in the region of Sulaimani city

| Group number | Sampling areas | Number of sampled sites | Description |
|-----------------|--------------------------|-------------------------|--|
| Non-urban soils | | | |
| 1 | Remote areas | 10 | Grassland sites in mountainous regions away from the urban area |
| 2 | Arable lands | 16 | Long-term cultivated agricultural fields in Sulaimani region |
| 3 | River upstream | 4 | Sites at Sarchnar and Qiliasan River banks upstream of the city |
| Urban soils | | | |
| 4 | River downstream | 5 | Sites at Tanjero River southern bank downstream of the city |
| 5 | Parks | 5 | Soils from flowerbeds and lawns of several public parks distributed in the city |
| 6 | Low traffic roads | 6 | Soils from shoulders and median strip of streets of traffic volume <250 vehicles h ^{-1a} |
| 7 | Semi-heavy traffic roads | 7 | Soils from shoulders and median strip of streets of traffic volume 500–1000 vehicles h ^{-1a} |
| 8 | Heavy traffic roads | 20 | Soils from shoulders and median strip of streets of traffic volume 1000–2000 vehicles h ^{-1a} |
| 9 | Industrial areas | 10 | Industrial areas (Sekariez, Asngarakan) in southern part of the city |
| 10 | Waste disposal | 7 | Main disposal area for unsorted waste (Slwienki Tanjero) |
| 11 | War affected | 2 | Soils from Halabja and Goptapa bombarded in 1988 with chemical weapons |

^a Traffic volume derived from data of Majid (2011)

Exchangeable Ca, K, Mg and Na were extracted with 1 M NH₄Cl solution; potential cation exchange capacity (CEC) was investigated by percolating soil samples with BaCl₂–triethanolamine, buffered at pH 8.1. For Na, the exchangeable sodium percentage (ESP) was calculated from that data. Aluminum, Fe and Mn were extracted from pedogenic oxides with 1 M ammonium oxalate. All elemental analysis was done using atomic absorption spectrometry (ContrAA 700 High-Resolution Continuum Source FI plus AA-240 Graphite AAS, Varian, Darmstadt, Germany). The total content of carbon and nitrogen was measured using a EuroEA elemental analyzer (HekaTech, Wegberg, Germany). To distinguish organic C (OC) from inorganic carbonate C (IC), soil samples were additionally analyzed after pretreatment to remove carbonate C. Briefly, 200 mg pulverized soil (dry mass) was treated with 200 mL 0.22 N HCl and then suspended with an Ultra-Turrax homogenizer (IKA, Staufen, Germany) for 3 min. Non-purgeable organic carbon (NPOC) was analyzed from this suspension with a Shimadzu TOC-V analyzer (Shimadzu, Duisburg, Germany), and data were used to calculate IC. Quality of measured data was proven by parallel, repeated analysis of certified soil samples (see Supplementary Material).

Determination of PTEs and PAHs

The total amount of the PTEs Cd, Cu, Pb and Zn was determined by acid digestion using pressure digestion

vessels (DAB-2, Berghof, Eningen, Germany). Briefly, 0.2 g of soil was digested with 3 mL 65 % HNO₃ and 1 mL H₂O₂ for 6 h at 150 °C. Additionally, the mobile fraction of the PTEs was extracted with 1 M NH₄NO₃ by shaking 2 g soil in 50 mL solution on an end-over-end shaker for 24 h. After centrifugation and filtration, samples were stabilized by addition of 0.5 mL concentrated HNO₃ (Zeien and Brümmer 1989). Both total and mobile PTE contents were determined with atomic absorption spectrometry (ContrAA 700 High-Resolution Continuum Source FI plus AA-240 Graphite AAS, Varian, Darmstadt, Germany) using flame AAS (Cu, Pb and Zn) or graphite furnace AAS (Cd). Limits of quantification (LOQ) for Cd, Cu, Pb and Zn were 0.05, 2.0, 2.5 and 5.0 mg kg⁻¹. All analyses have been done in duplicate. To validate the accuracy of the PTE analysis, standard samples were investigated in parallel (see Supplementary Material). Reported contents <LOQ resulted from averaging data >LOQ and data <LOQ, the latter treated as zero.

The PAHs were extracted from soil using a Dionex ASE 350 Accelerated Solvent Extraction system (Thermo Fisher Scientific, Dreieich, Germany) by two sequential cycles of acetone (Roth, Karlsruhe, Germany) heated to 105 °C for 40 min. After clean-up using Chromabond SiOH cartridges (Macherey–Nagel, Düren, Germany), acetone was evaporated to about 1 mL using a rotary evaporator before samples were completely dried by an N₂ stream. The PAHs were redissolved in 1 mL hexane (Roth, Karlsruhe, Germany).

Analysis was performed by gas chromatography–mass spectrometry (Agilent 6890 GC system with Agilent 5973 MS detector, Agilent Technologies, Waldbronn, Germany) using an Optima 5MS-0.25 μm, 30 m × 0.25 mm capillary column (Macherey–Nagel, Düren, Germany) as stationary phase. Benzo[a]anthracene-d12 was used as internal standard, and external calibration was done using a PAH standard mixture of 16 PAH according to US-EPA, both from LGC Standards (Wesel, Germany). Recovery rate of PAHs ranged from 73 % for phenanthrene to 103 % for pyrene but was low for naphthalene with 47 %.

Statistical methods and calculation of pollution indices

All results are presented as arithmetic means of replicate analyses. Statistical analyses were carried out using the SPSS 18.0 software package (IBM Deutschland, Ehningen, Germany). Significant differences among groups were calculated using the Duncan’s test and *t* test. Bivariate correlation between total contents of PTEs and soil properties was determined calculating the Pearson correlation coefficient and two-sided significance. The overall diversity in soil chemical characteristics was tested using unrotated principal component analysis (PCA). The soil properties listed in Table 2 but without soil textural properties were tested as factors. The KMO measure was mediocre (0.658), showing the overall suitability of the data for PCA.

Accumulation factors were calculated from the contents of PTEs determined in three soil layers of different depths. This was done by normalizing the content in one layer to the content in the corresponding deepest layer 3.

From the data on PTEs, seven different pollution indices were calculated. These were the contamination factor C_f^i (Håkanson 1980), which is defined as

$$C_f^i = C_n^i / C_0^i \tag{1}$$

Thereby, C_n^i represents the mean content in the investigated samples with the number *n* of the *i* elements investigated and C_0^i the mean content in reference samples having a preindustrial metal content. From this, the degree of contamination (C_d) was calculated according to Håkanson (1980):

$$C_d = \sum_{i=1}^{i=n} (C_f^i) \tag{2}$$

The modified degree of contamination (mC_d) was derived using the equation form Abraham and Parker (2008):

$$mC_d = \sum_{i=1}^{i=n} (C_f^i) / n \tag{3}$$

with *n* the number of contaminants investigated.

Furthermore, the pollution load index (*PLI*) was calculated using the equation of Tomlinson et al. (1980):

$$PLI = \sqrt[n]{C_{f1}^i \times C_{f2}^i \times \dots \times C_{fn}^i} \tag{4}$$

as well as the geoaccumulation index (I_{geo} ; Müller 1969):

$$(I_{geo}) = \log_2(C_n / [1.5 \times B_n]) \tag{5}$$

with B_n being the geochemical background in the study area.

Alternatively to the geoaccumulation index, the enrichment factor (*EF*) was calculated using the local and global background content of Mn for normalization (Buat-Menard and Chesselet 1979):

$$EF = \left(\frac{C_{n,local} / Mn_{local\ background}}{C_{n,global} / Mn_{global\ background}} \right) \tag{6}$$

Mean contents of metals in reference samples in the study area ($C_0^i, Mn_{local\ background}$) were calculated using data from layer 3 (20–30 cm) of unpolluted soils of the arable sites, remote areas and river soils upstream the city, which resulted in contents (mg kg⁻¹) of 20.4 for Pb, 25.8 for Cu, 110.0 for Zn and 391.0 for Mn. The contents of Cd in samples from layers 3 were extremely low and in many samples <LOQ. Hence, the local Cd background was calculated as the mean content from unpolluted layer 1 of non-urban soils. The resulting content of 0.093 mg kg⁻¹ matched the global Cd background of 0.098 mg kg⁻¹ reported by Taylor and McLennan (1985, 1995). The latter data on Cd as well as on Pb, Cu, Zn and Mn (17, 25, 71, 540 mg kg⁻¹; Taylor and McLennan 1985, 1995) were used as geochemical background contents (B_n) to calculate I_{geo} and *EF* for the four PTEs.

Lastly, the toxicity index (*TI*) was calculated, which assesses the toxic relevance of PTE contents (Azarbad et al. 2013):

$$TI = \sum_{i=1}^{i=n} (C_n^i / EC_{50i}) \tag{7}$$

The EC_{50} values for PTEs were taken from Welp (1999) who determined adverse effects on the dehydrogenase activity of the soil microbial community in a loamy Luvisol of pH 7. Hence, EC_{50} values should be applicable to the similar soils investigated in this study. The reported EC_{50} values (mg kg⁻¹) are 90 for Cd, 35 for Cu, 652 for Pb and 115 for Zn (Welp 1999).

Results and discussion

General soil properties

The fine soil samples (<2 mm) from urban and non-urban sites of the region of Sulaimani were largely similar in soil texture ranging from silty clay loam (SiCL) to silty clay (SiC)

Table 2 Mean values and standard deviations (in parenthesis) of selected basic properties of 91 topsoil samples from sites of different land use in the city and surroundings of Sulaimani, Kurdistan. Significant differences between sites are indicated by letters (Duncan test, $p < 0.05$)

| Sampling area | Remote areas | Arable lands | River upstream | River downstream | Parks | Traffic roads | | | | Industrial areas | Waste disposal | War affected |
|---|---------------------------------------|------------------|------------------------|----------------------------------|---------------|----------------|------------------------|------------------------|---------------------------------|------------------------|---------------------------------------|------------------------|
| | | | | | | 10 | 16 | 4 | 4 | | | |
| # of sampling sites | 10 | 16 | 4 | 4 | 5 | 6 | 7 | 7 | 20 | 10 | 7 | 2 |
| Soil texture | Silty clay, (sandy clay) ¹ | Loam, silty clay | Sandy clay, silty clay | Sandy to silty loam ² | Silty clay | Silty clay | Silty clay, silty clay | Silty clay, silty clay | Sandy clay to clay ² | Silty loam, silty clay | Sandy loam to silty clay ² | Sandy clay, silty clay |
| Fract. > 2 mm (%) | 10.9ab (9.0) | 7.4a (8.4) | 90.0ef (8.4) | 92.8f (10.6) | 58.5de (43.0) | 16.9abc (8.5) | 41.4abcd (32.7) | 45.8 cd (36.4) | 7.7 (7.6) | 57.9de (34.1) | 6.1a (3.9) | 79.1ef (20.0) |
| pH H ₂ O | 7.7 (0.11) | 7.5 (0.18) | 7.8 (0.13) | 7.7 (0.05) | 7.8 (0.06) | 7.7 (0.05) | 7.6 (0.16) | 7.7 (0.11) | 7.7 (0.11) | 7.6 (0.14) | 7.6 (0.09) | 7.8 (0.09) |
| IC (%) | 2.40ab (1.0) | 1.31a (1.0) | 4.18c (1.1) | 5.44 cd (0.4) | 4.38c (0.3) | 5.24 cd (1.2) | 6.01d (1.5) | 4.82c (1.1) | 4.82c (1.1) | 4.49c (0.9) | 2.70b (0.8) | 3.85 cd (0.2) |
| OC (%) | 1.07a (0.3) | 1.37a (0.4) | 0.66a (0.3) | 0.67a (0.2) | 1.36a (0.7) | 0.91a (0.7) | 0.56a (0.4) | 1.33a (1.0) | 1.33a (1.0) | 3.24b (2.0) | 1.23a (0.9) | 1.48a (1.2) |
| Total N (%) | 0.15abc (0.05) | 0.32d (0.11) | 0.08ab (0.05) | 0.07a (0.02) | 0.19c (0.08) | 0.11abc (0.05) | 0.18bc (0.09) | 0.15abc (0.07) | 0.15abc (0.07) | 0.16abc (0.06) | 0.13abc (0.10) | 0.23c (0.15) |
| C/N | 7.1a (0.8) | 5.1a (3.2) | 9.3a (0.7) | 10.0a (1.1) | 7.0a (0.8) | 7.5a (4.1) | 3.4a (2.3) | 8.5a (4.2) | 8.5a (4.2) | 19.5b (0.7) | 9.5a (0.9) | 6.1a (1.7) |
| CEC (cmol _c kg ⁻¹) | 43.10c (4.2) | 37.14abc (12.4) | 29.37ab (4.8) | 27.06a (2.6) | 37.94bc (3.2) | 32.53ab (6.6) | 29.32ab (7.9) | 30.98ab (9.2) | 30.98ab (9.2) | 32.94ab (8.1) | 44.80c (7.3) | 28.74a (0.2) |
| ESP (%) | 0.20a (0.5) | 0.29a (0.6) | 0.30a (0.4) | 0.62b (0.3) | 0.37ab (0.7) | 0.36ab (1.8) | 0.38ab (1.8) | 0.48ab (1.7) | 0.48ab (1.7) | 0.46ab (1.9) | 0.46ab (1.9) | 0.38ab (0.5) |
| EC (mS cm ⁻¹) | 0.51 (0.02) | 0.75 (0.06) | 0.64 (0.06) | 0.82 (0.39) | 0.92 (0.07) | 1.81 (0.07) | 1.33 (0.14) | 1.89 (0.32) | 1.89 (0.32) | 2.03 (0.20) | 1.75 (0.37) | 1.08 (0.51) |
| Fe _{ox} (g kg ⁻¹) | 0.89a (1.8) | 1.49a (5.8) | 0.88a (4.1) | 2.21a (3.3) | 0.89a (3.1) | 0.89a (2.5) | 1.07a (3.0) | 1.17a (0.4) | 1.17a (0.4) | 4.01a (78.1) | 0.84a (3.1) | 0.38b (2.4) |
| Al _{ox} (g kg ⁻¹) | 1.55d (3.2) | 1.46 cd (7.4) | 0.58a (2.6) | 0.85ab (2.6) | 0.81ab (1.7) | 1.01abc (0.3) | 1.04abc (3.2) | 1.02abc (2.7) | 1.02abc (2.7) | 1.00abc (1.6) | 1.35bcd (0.2) | 0.97abc (0.1) |
| Mn _{ox} (g kg ⁻¹) | 0.38b (1.0) | 0.68c (2.6) | 0.26ab (1.0) | 0.26ab (1.2) | 0.26ab (0.9) | 0.41b (0.1) | 0.32ab (0.4) | 0.31ab (1.0) | 0.31ab (1.0) | 0.32ab (1.3) | 0.35ab (0.5) | 0.16a (0.1) |

¹ Texture class of one out of 10 soil samples² Texture classes of several soils ranged between those named in the table

IC inorganic carbon from calcite and dolomite

with clay contents of 35 to 55 %, except for the river soils at Qilianshan and Tanjero River and soils from the Penjwin high plains area, where the texture was identified as loamy sand (LSa) and loam (L), respectively (Table 2). Overall, this corresponds to previous findings of Buringh (1960) and FAO (2003). The topsoil samples collected at the remote mountainous grassland and from arable land had on average 9 % by mass of rock fragments >2 mm. By comparison, river soils and urban soils contained much higher portions of rock fragments with an overall average of 91.4 and 42.0 % by mass, respectively (compare Table 2). However, rock fragments in river soils were round pebbles from fluvial sedimentation, while urban soils contained mostly angular gravel. An elevated content of coarse material is typical for many urban soils (Blume 1996; Jim 1998) and most likely originates from anthropogenic activities such as soil removal and leveling, resulting in markedly modified and/or shallower soils that are more affected by underlying rock debris (Hiller and Meuser 1998). These differences between urban and non-urban soils were further confirmed by soil chemical analyses.

Data on pH, IC, OC, total N, C/N ratio, CEC, ESP, EC and oxalate soluble Fe-, Al- and Mn-oxides are listed in Table 2. Further descriptive statistical parameters can be found in Table S1 (Supplementary Material). Due to soil formation from carbonate rock and the semiarid climate, all soils were strongly to extremely calcareous according to FAO classification (Jahn et al. 2006) with average IC contents between 1.31 and 6.01 % being equivalent to a calcium carbonate content between 11 and 51 %. Significantly lowest IC contents were found in non-urban arable and remote grassland soils and highest contents in roadside soils. Correspondingly, pH values of roadside soils were high, ranging on average between 7.5 and 7.8.

Generally, OC content was low in natural soils and medium in arable soils of the region as it was earlier reported by FAO (2003). The OC contents were somewhat, yet nonsignificantly lower in urban soils compared to non-urban soils (Table 2). In contrast, OC contents were significantly higher in soils from the industrial sites with on average 3.24 %. This was combined with a much higher C/N ratio of 19.5 compared to a C/N ratio of 7.3 as a mean for all other soils. This indicates that part of OC was most likely derived from carbonaceous material such as coal and ashes. The C/N ratio of these materials is typically very high reaching values of >500 (Cayuela et al. 2014).

The CEC of soils from different sampling areas ranged between 27 and 45 cmol_c kg⁻¹ (Table 2). The CEC of the non-urban soils was at the upper end of the range, and CEC of soils from remote mountainous grassland sites was significantly higher than that of most urban soils. The CEC of arable soils varied widely so that no significant differences were obtained.

Electric conductivity (EC) averaged for the soil groups ranged between 0.51 and 2.03 mS cm⁻¹ (Table 2) and did not indicate salt accumulation in the soils confirming previous reports (Buringh 1960; FAO 2003). Yet, it was highly significantly larger ($p < 0.01$) by a factor of 1.7 in urban soils compared to non-urban soils. Also, the exchangeable sodium percentage (ESP) was highly significantly ($p < 0.01$) increased in soils from roadsides, industrial and waste disposal areas by a factor of 2.8, confirming the findings on EC. Enrichment of Na in roadside soils is typically due to the use of deicing salts (Zehetner et al. 2009), which is not relevant under the climatic conditions investigated in this study. Instead, it might be assigned to other sources such as abrasion dust from brakes (McKenzie et al. 2009), wastewater disposal and industry emissions (Han et al. 2007). Additionally, it is assumed that higher salt content in urban soils under a semiarid climate as in Sulaimani is also partly due to changes in the water balance of the soilscape. Soil sealing and compaction in urban areas strongly affect water infiltration and percolation (Scalenghe and Marsan 2009; Wong et al. 2006), possibly resulting in higher salt retention in the soils. This assumption was evidenced by significant depth gradients in EC. The total mean of EC declined from 0.76 mS cm⁻¹ in 0–5 cm soil depth to 0.53 mS cm⁻¹ in 5–10 cm soil depth and 0.48 mS cm⁻¹ in 20–30 cm soil depth (detailed data not shown).

The non-urban soils had the highest contents of Mn_{ox} and Al_{ox} with differences being significant for some soil groups, whereas differences in the content of Fe_{ox} were not significant (Table 2). Yet, standard deviation for Fe_{ox} contents was highest in soils from industrial areas (Table 2), and in one soil sample from the industrial areas, the content of Fe_{ox} was extremely high with 261 mg kg⁻¹ (data not shown). It is suggested that these heterogeneous and partly high contents originated from industrial point-source contamination.

Combining the results on higher rock fragment fractions, the trend to lower OC, in part higher EC, ESP and CEC indicated that urban soils of the Sulaimani region were altered by anthropogenic activities. To further prove this, soil chemical data were evaluated using PCA. The first three principal components had eigenvalues of 3.0, 2.4 and 1.5, explaining 62.7 % of the total variance. Results in Fig. 2 show, although data scattered considerably, that PCA very much separated urban and non-urban soils into different clusters. This is mostly attributed to differences in Mn_{ox}, IC, total N and Al_{ox}, loading the most on PC 1. Partly, the soil samples from the vicinity of the waste disposal site formed a third cluster, lying in between the two above-mentioned clusters. This corresponds to the location of the site within arable fields, so that it combines features of both urban and non-urban soils. The river soils

Fig. 2 Principal component analysis of general soil properties of non-urban and urban soils from the Sulaimani region. Lines indicate the boundaries within which soils from sampling areas with different anthropogenic impact are clustered, i.e., non-urban arable lands and remote areas as well as urban soils and soils from a waste disposal site. The factor loadings are shown by the inset figure

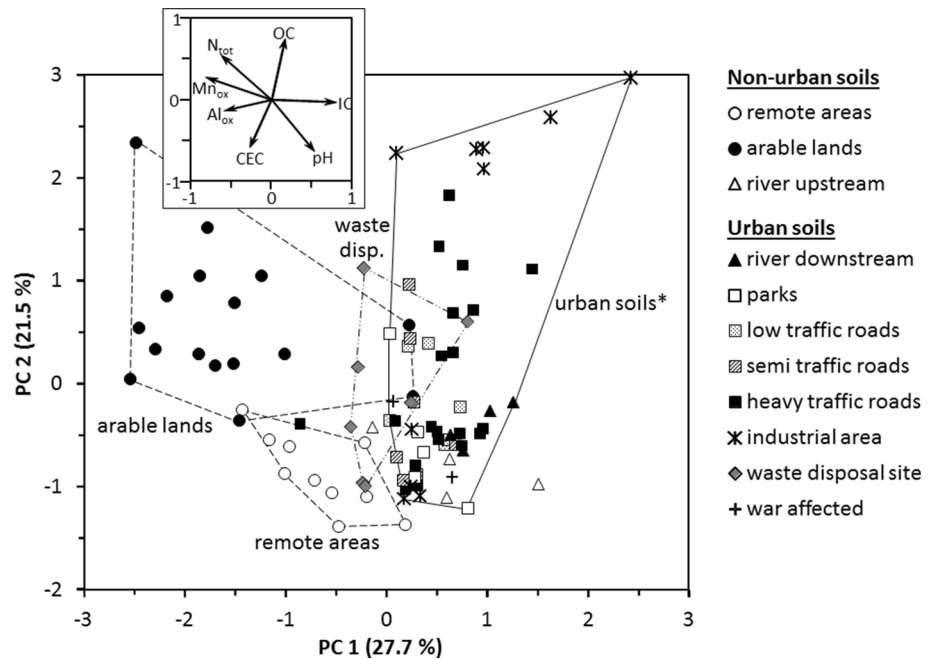


Table 3 Mean values with minima and maxima in parenthesis of total PTE contents (Cd, Pb, Cu, Zn; mg kg^{-1}) in 0–5 cm layers of soils from areas with different usage intensity and pollution risk of the region and city of Sulaimani. Significant differences in the content of a PTE between sampling areas are indicated by letters (Duncan's test, $p < 0.05$)

| Sampling area | Cd (mg kg^{-1}) | Pb (mg kg^{-1}) | Cu (mg kg^{-1}) | Zn (mg kg^{-1}) |
|--------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Remote areas | 0.08 (ND-0.32) | 17.6a (5.77–36.3) | 14.8 (2.0–37.0) | – |
| Arable lands | 0.22 (ND-0.56) | 7.41a (4.03–15.5) | 29.9 (24.0–34.0) | 107a (97.8–119) |
| River upstream | ND | 10.1a (7.77–11.7) | ND | – |
| Non-urban soils mean | 0.100 | 11.7 | 14.9 | 107 |
| River downstream | ND | 14.3a (9.40–18.6) | ND | – |
| Parks | 0.09 (ND-0.25) | 23.1a (18.2–30.8) | 22.3 | 114a |
| Low traffic roads | 0.33 (0.28–0.38) | 78.9a (24.4–133) | 25.0 (22.3–27.7) | 104a (102–106) |
| Semi-heavy traffic roads | 0.24 (ND-0.52) | 59.4a (22.1–111) | 33.8 (28.8–41.1) | 276b (90.6–456) |
| Heavy traffic roads | 0.54 (ND-4.31) | 71.1a (18.7–209) | 50.5 (21.1–172) | 159ab (84.0–248) |
| Industrial areas | 1.26 (ND-7.68) | 148b (12.6–365) | 391 (19.6–1598) | 242b (49.9–484) |
| Waste disposal | 0.29 (0.19–0.49) | 6.88a (3.56–13.9) | 27.5 (20.0–35.5) | 80.7a (67.2–93.3) |
| War-affected sites | 0.06 (ND-0.12) | 12.8a (11.3–14.2) | – | – |
| Urban soils mean | 0.351 | 51.8 | 78.6 | 163 |
| Precautionary values | 1.5 | 100 | 60 | 200 |
| Permissible limits | 1.0 | 20 | 20 | 50 |
| Recommended values | 0.4 | 35 | 19 | 106 |

ND not detectable, content below limit of detection

–, no data available

Precautionary values for clay soils; according to German Federal Soil Protection Regulation (BBodSchV 1999)

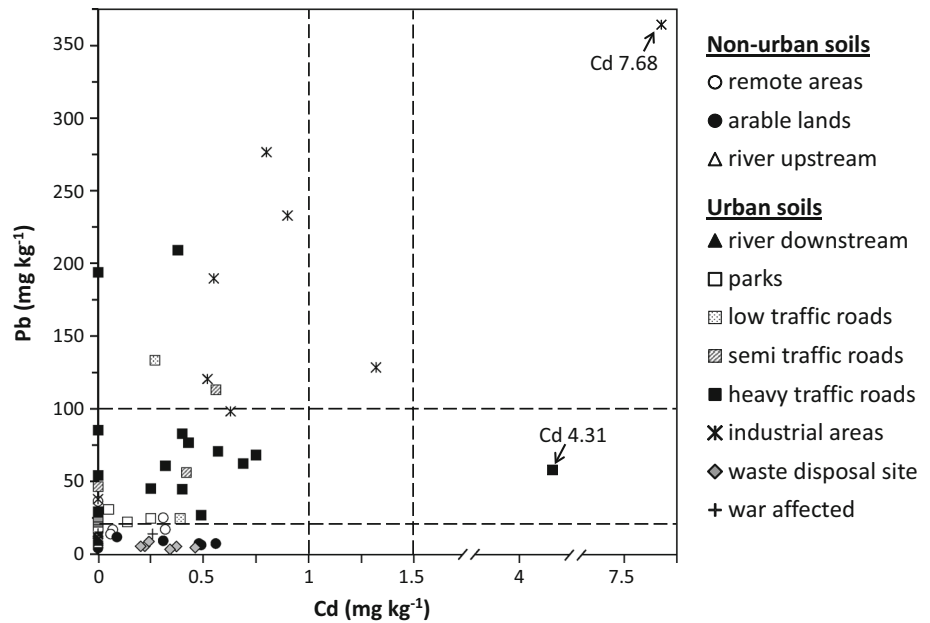
Permissible limits according to Kloke (1980)

Recommended values according to National Institute of Standard Technology (NIST 2013)

from upstream of the city were considered as 'non-urban' but had chemical properties differing from those of the other non-urban soils and were not separated from urban soils by PC 1 (Fig. 2). This is related to the very different composition of these semiterrestrial soils compared to the otherwise terrestrial soils analyzed in this study. The OC

content, pH and CEC were the properties loading the most on PC 2. The PC 2 further separated arable soils from remote grassland soils, river soils upstream the city from those downstream and most of the soils from the industrial areas as well as some of the heavy traffic roadside soils from all other soils. In total, PCA substantiated the

Fig. 3 Total contents of Cd and Pb in soils of Sulaimani region from sampling areas with different anthropogenic impact. Dashed lines indicate permissible limits according to Kloke (1980) and precautionary values according to German Federal Soil Protection Regulation (BBodSchV, 1999). Note the broken x-axis



different composition of urban and non-urban soils, which is most likely due to anthropogenic urban activities.

Contents of Cd, Pb, Cu, Zn and PAHs in urban and non-urban soils

Total contents of Cd, Pb, Cu and Zn in the 0–5 cm surface layer of soils from the different sampling areas in and around Sulaimani city are listed in Table 3. Further descriptive statistical parameters are presented in Table S2 (Supplementary Material). Total contents ranged in non-urban soils from non-detectable contents (ND) to 0.56 mg kg⁻¹ for Cd, 4.03 to 36.3 mg kg⁻¹ for Pb, ND to 37.0 mg kg⁻¹ for Cu and 97.8 to 119 mg kg⁻¹ for Zn. The ranges cover natural background values previously reported for soils from the Sulaimani area and comparable clayey and calcareous soils (cited in Möller et al. 2005; Kabata-Pendias 2010).

Generally, PTE contents tended to be higher in urban compared to non-urban soils, confirming reports from other cities, for example, reviewed by Ajmone-Marsan and Biasioli (2010) and Luo et al. (2012). This is shown in Fig. 3 as an example of Cd and Pb. Furthermore, a tendency for higher content of one PTE in the presence of the other was seen (Fig. 3). Contents of all four PTEs were significantly, positively correlated ($p < 0.05$), except for Cd with Cu and Zn in urban soils (Table S3 in Supplementary Material). Highest contents of all four PTEs were determined in soils from the industrial areas. Despite the wide ranges, and thus large standard deviations of mean values, these differences to non-urban soils were significant for Pb and Zn in soils from the industrial areas and for Zn

in soils from semi-heavy traffic roads (Table 3). The higher contents within the ranges measured for PTEs in soils from the industrial areas and heavy traffic roads (Cd, Cu, Pb, Zn), semi-heavy traffic roads (Pb, Zn) as well as low traffic roads (Pb) exceeded precautionary values for these PTEs (Table 3), for example, as listed in the German Federal Soil Protection Regulation (BBodSchV 1999), while similar regulations are not yet existent in Iraq. Mean content values of Pb, Cu and Zn, but not of Cd, of the urban soils were higher than the permissible limits set up by Kloke (1980, Table 3). Furthermore, urban mean contents of the four PTEs were similar for Sulaimani and those reported for, for example, Bangkok, Damascus and Karachi, as well as Ehu Town, Wuxi City, a rapid urbanization area in Eastern China (Karim and Qureshi 2014; Li et al. 2014; Möller et al. 2005; Wilcke et al. 1998). Yet, metal contents were substantially lower compared to many other cities in Europe, South America and China with population ≥ 1 million (Ajmone-Marsan and Biasioli 2010; Imperato et al. 2003; Luo et al. 2012; Trujillo-González et al. 2016; Wei and Yang 2010). This is explained by a short accumulation time in cities with a short history of industrialization and population growth (Li et al. 2014; Wilcke et al. 1999a; Wilcke et al. 1998) as it applies for Sulaimani as well.

Ranking the different sampled areas by their contents of the four PTEs resulted in the following sequence of increasing contamination: river soils upstream (Qiliasan stream) < river soils downstream (Tanjero River) < remote areas < war-affected sites < waste disposal < arable lands < parks < low traffic roads < semi-heavy traffic roads < heavy traffic roads < industrial areas. This clearly indicates anthropogenic pollution of the urban soils, which

increases with the extent of anthropogenic activity, i.e., traffic volume and industrial emissions. Higher soil pollution is typically found along major traffic pathways and at industrial sites (Imperato et al. 2003; Lee et al. 2006; Peña-Fernández et al. 2015; Wilcke et al. 1998) compared to parks and suburban areas (Gu et al. 2016; Yan et al. 2015). In particular, the use of Pb as fuel additive exposes soils in the proximity of roads to Pb contamination (Ajmone-Marsan and Biasioli 2010); fuel with Pb additive is still in use in Iraq (UNEP 2015) leading to very high maximum contents in roadside soils of Sulaimani.

Sequences of PTE contents in soils from different areas varied between elements, enabling further suggestion of possible contamination sources. Contents of Cu and especially Zn were also high in arable soils compared to urban soils (Table 3). Both Cu and Zn are micronutrients and are especially contained in manure and sewage sludge fertilized to soil (Ogiyama et al. 2005). Thus, arable soils frequently have elevated contents of Cu and Zn but low contents of Cd and Pb with the reported ranges matching those found in this study (De Temmerman et al. 2003; Römkens and Salomons 1998). Soils at the waste disposal site Slwienki Tanjero as possible point source for contamination were sampled in different distances between 5 and 100 m. The soil content of Cu but not of the other PTEs significantly declined with increasing distance, and Cu content and distance were negatively correlated with $r = -0.78$ ($p < 0.05$).

The mobility of PTEs was rather low as was determined by extraction with 1 M NH_4NO_3 , representing the mobile fraction (Pueyo et al. 2004). The NH_4NO_3 extractable contents of Cd, being the most mobile of the four PTEs, were above the limit of detection in only 20 % of the samples with contents $\leq 0.31 \text{ mg kg}^{-1}$ (data not shown). This is explained by the strong sorptive properties of the calcareous, clayey and mostly montmorillonitic soils at Sulaimani (Al-Rawi et al. 1969) with high pH (Table 2). In contrast, in less calcareous urban soils of other cities, Cd was mainly recovered from the easily exchangeable fractions (Ajmone-Marsan and Biasioli 2010). The even stronger immobilization of Pb, Cu and Zn found in this study was in accordance with the previous reports, being attributed to fixation of Pb and Zn in metal oxides and residual mineral phases and of Cu mainly in organic forms (Imperato et al. 2003; Wilcke et al. 1998; Yang et al. 2006).

The possible soil contamination with PAHs was investigated on example of six selected samples from the industrial areas and heavy traffic roadside soils that exhibited clearly altered chemical properties such as increased PTE content. The PAH content was compared with that of four randomly selected non-urban soils. Only in one sample from an industrial site, contents of four out

of 16 PAHs were determined that exceeded the analytical LOQ [content (mg kg^{-1}) in parentheses]: naphthalene (2.790), fluoranthene (0.200), phenanthrene (0.229) and pyrene (0.165). Additionally, the sample exhibited the highest content of Fe_{ox} , total Cd and Pb of all samples indicating a strong and complex contamination due to industrial emissions. PAH contents determined in this study were substantially lower than those previously reported for other urban areas (Wilcke 2007). The finding furthermore confirms Wilcke (2007), who reported also for PAHs that the contamination level in areas without a long history of environmental contamination, although being heavily industrialized and urbanized in the last years, is considerably low. Furthermore, high volatilization during dry season and increased degradation during wet season (Wilcke et al. 1999a), which especially applies to the semiarid climate at Sulaimani, might have contributed to this result.

Depth distribution of Cd, Pb, Cu and Zn

The vertical distribution of the four PTEs was further investigated for selected subsets of 27 (Cd) to 45 (Pb) urban sampling sites representing different anthropogenic impact. In addition, samples from eight non-urban sites and five park sites were investigated for Pb. Total PTE contents were analyzed in three different layers from the topsoil horizon, i.e., 0–5 cm (layer 1), 5–10 cm (layer 2) and 20–30 cm (layer 3). In the vast majority of all soils, PTE contents in the upper layers were higher compared to the lower layers, whose differences were mostly significant (Fig. 4). However, it may be noted that results from statistical analysis were different, when data from all sampling areas were combined (Table 4). PTE contents in the different layers were mostly not correlated, except for Pb (Table 4), indicating that type and age of contamination and progress of transport into the soil depth might largely differ among sites.

The stronger enrichment of PTEs in 0–5 cm soil depth was further evidenced by calculated accumulation factors (Table 4) and confirmed that PTEs in urban soils of Sulaimani originated from anthropogenic pollution adding to the geogenic background content (Kabata-Pendias 2010; Luo et al. 2012). Accumulation factors declined with soil depths and ranged from 57.9 to 1.2 (Table 4). Accumulation of Cd was especially strong, though on a low background content level with contents in layer 3 being mostly at or below the LOQ (Fig. 4), and can be interpreted as an indicator of higher emissions (Cui et al. 2011). The lower relative accumulation of Pb, Cu and Zn is explained by higher natural background of these elements as is usually observed in the Kurdistan region (Kabata-Pendias 2010; Maleki et al. 2014; Parizanganeh et al. 2012).

Anthropogenic contamination was especially found for Cd and Pb as indicated by most significant differences between layers. Both PTEs are typical pollutants from car traffic (Ajmone-Marsan and Biasioli 2010). Accumulation was less significant for Cu and Zn; these elements are typical pollutants from metal industry (Kabata-Pendias 2010). Correspondingly, Cu contamination was in part extremely high at the industrial areas investigated in this study (Table 3 and Fig. 4). It is assumed that accumulation of PTEs in the 0–5 cm layer was intensified by the semiarid climate that also resulted in the accumulation of salt in layer 1 (EC in layer 1, 2, 3: 0.76, 0.53, 0.48 mS cm⁻¹).

It is all the more noteworthy that accumulation of Cd was significantly higher not only in layer 1 but also in layer 2 compared to layer 3 ($p < 0.01$; Table 4), while in contrast, Pb accumulation was mostly restricted to the top 0–5 cm (layer 1). It is assumed that Cd, exhibiting higher mobility than Pb (Ajmone-Marsan and Biasioli 2010), had been slightly transported into the soil with infiltrating water, even though low mobility was determined for the clayey, high-pH soils investigated in this study. The transport of Cd might have been promoted by the determined decline in OC and CEC in urban soils (Table 2). In contrast, transport through bioturbation or anthropogenic soil mixing processes would have resulted in similar depth distributions of Cd and Pb.

Assessment of PTE contamination

Different parameters were calculated to assess the contamination level and its ecological relevance in the area of the city of Sulaimani (Table 5). With the contamination factor (C_f ; Håkanson, 1980) and the index of geoaccumulation (I_{geo}), the contamination level is related to a local and a global background level, respectively, while the additional normalization to a typical geogenic element in the enrichment factor (EF ; Buat-Menard and Chesselet 1979) indicates enrichment beyond that from accumulation by rock weathering and can reflect metal enrichment on a long-term scale (Mohiuddin et al. 2010).

All three parameters show no or a very small level of contamination in the non-urban soils and the river soils downstream of the city of Sulaimani (Table 5). Values are in the lowest class, indicating uncontaminated soils or even element deficiency (EF). Some contents of PTEs were even below the detection level so that no data for I_{geo} and C_f could be calculated. Comparing the results for river soils upstream and downstream the city showed that until now, wastewater discharge or other urban activities have not led to contamination of the Tanjero river soils by PTEs. This seems not atypical, e.g., Mohiuddin et al. (2010) and Rabee et al. (2011) reported similarly low contamination and index values for sediments of Tsurumi River downstream

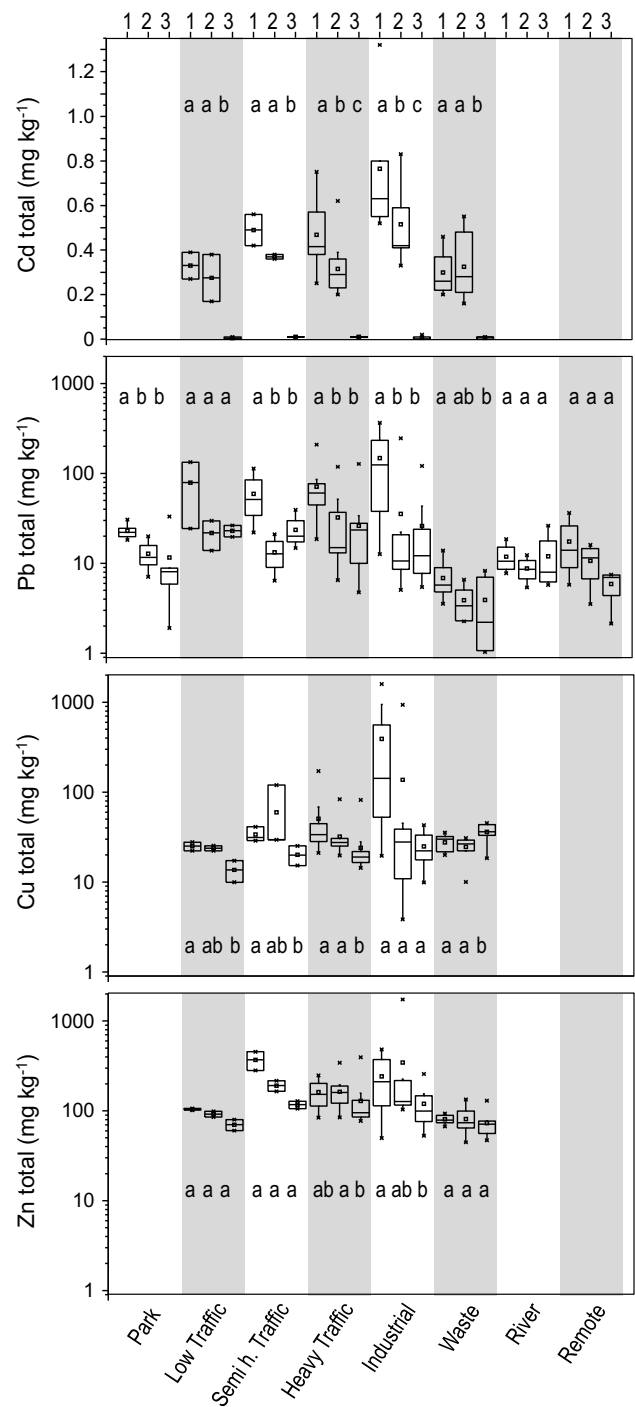


Fig. 4 Total contents of Cd, Pb, Cu and Zn in different depth layers of topsoil, i.e., 0–5 cm (layer 1), 5–10 cm (layer 2) and 20–30 cm (layer 3), from selected sampling sites of the studied area. Significant differences in PTE contents between layers are indicated by different lower-case letters ($p = 0.05$). Contents below the LOQ were calculated as average of data above and below the LOQ; the latter data were considered as zero

of Yokohama, Japan, and of Tigris River in the Baghdad region, respectively. However, moderate contamination with Cd, Cu and Zn was determined for arable soils and EF

Table 4 PTE content (mg kg^{-1}) in different soil layers, averaged for all investigated urban sampling sites and areas, standard deviation and ratio of accumulation in ith layer related to layer 20–30 cm; statistical comparison for significant differences and correlation of PTE content in different soil layers

| | Soil layer; Soil depth (cm) | Element content mg kg^{-1} | Standard deviation | Accumulation C_i/C_{20-30} | Statistical comparison | Paired t test | Correlation coefficient r |
|----|-----------------------------|-------------------------------------|--------------------|------------------------------|------------------------|-----------------|-----------------------------|
| Cd | 1; 0–5 | 0.461 | 0.237 | 57.9 | 1–2 | 3.27** | 0.31 n.s. ^a |
| | 2; 5–10 | 0.352 | 0.156 | 44.2 | 1–3 | 8.56** | 0.17 n.s. |
| | 3; 20–30 | 0.008 ^b | 0.004 | 1.0 | 2–3 | 9.98** | 0.63** |
| Pb | 1; 0–5 | 70.84 | 79.29 | 3.5 | 1–2 | 4.86** | 0.60** |
| | 2; 5–10 | 23.96 | 40.65 | 1.2 | 1–3 | 4.94** | 0.59** |
| | 3; 20–30 | 20.39 | 25.00 | 1.0 | 2–3 | 0.58 n.s. | 0.30* |
| Cu | 1; 0–5 | 122.9 | 305.42 | 4.8 | 1–2 | 1.10 n.s. | –0.02 n.s. |
| | 2; 5–10 | 57.09 | 156.74 | 2.2 | 1–3 | 1.87 n.s. | 0.15 n.s. |
| | 3; 20–30 | 25.77 | 14.00 | 1.0 | 2–3 | 1.19 n.s. | 0.18 n.s. |
| Zn | 1; 0–5 | 173.41 | 114.70 | 1.6 | 1–2 | 1.15 n.s. | 0.06 n.s. |
| | 2; 5–10 | 188.23 | 288.37 | 1.7 | 1–3 | 1.87 n.s. | 0.42* |
| | 3; 20–30 | 110.11 | 67.00 | 1.0 | 2–3 | 1.19 n.s. | 0.29 n.s. |

^a n.s. not significant; level of significance of paired t test and correlation: * $p = 0.05$; ** $p = 0.01$

^b Average of data above and below the limit of quantification; the latter data were considered as zero

even indicated significant contamination with Cd. As has been already discussed, the contamination with Cu and Zn might be due to the application of manure and/or sewage sludge (Ogiyama et al. 2005), while phosphorous fertilizers are a typical source of Cd in arable soil (Blume et al. 2010). All non-urban soils showed no contamination with Pb, which confirms that this is a distinctive pollutant in urban soils.

The three parameters consistently indicated a clear and in part very high contamination level of Cd, Pb and Cu in urban soils (Table 5). Indices increased from soils of low and semi-heavy traffic roads to high traffic roads and industrial areas. Contamination in roadside soils was classified as ‘moderate’ for Cu and Zn, and as ‘moderate’ to ‘considerable’ (C_f) and ‘significant’ (EF) for Cd and Pb. Correspondingly, enrichment was highest for Pb, Cd and Cu in soils from numerous Chinese cities (Luo et al. 2012; Wei and Yang 2010). Contamination of soils from the industrial sites was classified as ‘moderate to heavy’ and ‘heavy’ (I_{geo}), and ‘significant’ to ‘very high’ (C_f , EF) for Cd, Pb and Cu, while Zn contamination was categorized as ‘moderate.’ It must be noted that the classification of soils from the industrial areas very much depended on the very high contamination of some samples, while other samples from that areas were much less contaminated (Table 3). Also, soils of the waste disposal site showed moderately increased contents of Cu and Cd (Table 5). Since these increases are clearly different from those in arable soils, it must be concluded that the contamination originates from

the waste disposal. In total, the assessment stresses the adverse effect of urban activities on the contamination status of soils. A comparable increase in soil contamination and derived indices was reported for the city of Dongguan, China, which similarly to Sulaimani underwent a rapid urbanization and industrialization in the past decades (Wu et al. 2015).

To assess the total contamination with all four PTEs, the degree of contamination (C_d), the modified degree of contamination (mC_d ; Håkanson 1980) and the pollution load index (PLI ; Tomlinson et al. 1980) were calculated. The two degrees of contamination underpin the increased soil contamination with increased anthropogenic activities. Yet, due to the integration of higher (especially Cd and Pb) and lower enrichment (especially Cu and Zn), the overall classification was mostly ‘low’ to ‘moderate,’ while it was ‘considerable’ and ‘high’ for soils from the industrial areas. Consistently, the PLI revealed that ‘a detailed study and monitoring’ is required for soils from the industrial areas.

The toxicity index (TI) is the ratio of the contaminant content to effective concentrations of the same metal (Stefanowicz et al. 2008) and is used as an estimate of the ecotoxic relevance of soil contamination. The TI of 3.38 for soils from the industrial areas (Table 5) indicates that a toxic contamination level has been reached and adverse effects on soil biota and respective ecosystem functions must be expected. TI values around 0.5 were calculated for most urban soils and arable soils of the Sulaimani region. Although this tells that the contamination level is only half

Table 5 Geo-accumulation indices (I_{geo} ; Müller 1969), enrichment factors (EF ; Buat-Menard and Chesselet 1979) and contamination factors (C_f^i ; Håkanson 1980) of Cd, Cu, Pb and Zn, and degree of contamination (C_d), modified degree of contamination (mC_d ;

Håkanson 1980), pollution load index (PLI ; Tomlinson et al. 1980) as well as toxicity index (TI ; Stefanowicz et al. 2008; Azarbad et al. 2013) of the PTE contamination in top layers of soils from areas with different usage intensity and pollution risk

| Remote areas | Cd | | | Pb | | | Cu | | | Zn | | | Cd + Pb + Cu + Zn | | | |
|--------------------------|-----------|------|---------|-----------|------|---------|-----------|------|---------|-----------|------|---------|-------------------|--------|-------|------|
| | I_{geo} | EF | C_f^i | I_{geo} | EF | C_f^i | I_{geo} | EF | C_f^i | I_{geo} | EF | C_f^i | C_d | mC_d | PLI | TI |
| Arable lands | -0.9 | 1 | 0.4 | -0.8 | 1 | 0.9 | -1.4 | 1 | 0.6 | - | - | - | 1.8 | 0.6 | 2.7 | 0.15 |
| River soil upstream | 1.2 | 5 | 1.7 | -1.0 | 1 | 0.4 | -0.4 | 2 | 1.2 | -0.6 | 2 | 1.0 | 4.2 | 1.0 | 18 | 0.55 |
| River soil downstream | ND | 0 | ND | -1.6 | 1 | 0.5 | ND | 0 | ND | - | - | - | 0.5 | 0.5 | 10 | 0.01 |
| Parks | ND | 0 | ND | -1.1 | 1 | 0.7 | ND | 0 | ND | - | - | - | 1.6 | 0.8 | 18 | 0.01 |
| Low traffic roads | -0.6 | 1 | 0.5 | -0.4 | 2 | 1.1 | -0.8 | 1 | 1.0 | -0.5 | 2 | 1.0 | 3.6 | 0.9 | 8.6 | 0.42 |
| Semi-heavy traffic roads | 1.2 | 5 | 1.7 | 1.4 | 6 | 3.9 | -0.6 | 2 | 1.3 | -0.7 | 1 | 0.9 | 7.8 | 2.0 | 17 | 0.36 |
| Heavy traffic roads | 0.8 | 3 | 1.3 | 1.0 | 5 | 2.9 | -0.2 | 0.5 | 0.3 | 0.7 | 4 | 2.5 | 7.0 | 1.7 | 13 | 0.50 |
| Industrial areas | 2.0 | 8 | 2.8 | 1.2 | 6 | 3.5 | 0.4 | 3 | 2.0 | -0.1 | 2 | 1.4 | 9.7 | 2.4 | 24 | 0.65 |
| Waste disposal | 3.2 | 18 | 6.6 | 2.3 | 12 | 7.3 | 3.3 | 22 | 15 | 0.6 | 3 | 2.2 | 31 | 7.8 | 65 | 3.38 |
| War-affected sites | 1.1 | 4 | 1.5 | -2.2 | 1 | 0.3 | -0.5 | 2 | 1.1 | -1.0 | 1 | 0.7 | 3.7 | 0.9 | 8.2 | 0.36 |
| | -0.2 | 2 | 0.6 | -1.3 | 1 | 0.6 | - | - | - | - | - | - | 1.3 | 0.6 | 1.2 | 0.01 |

I_{geo} classes (Müller 1969): $I_{geo} < 0$: uncontaminated; $0 < I_{geo} < 1$ uncontaminated to moderately contaminated; $1 \leq I_{geo} < 2$ moderately contaminated; $2 \leq I_{geo} < 3$: moderately to heavily contaminated; $3 \leq I_{geo} < 4$: heavily contaminated; $4 \leq I_{geo} < 5$: heavily to extremely contaminated; $I_{geo} > 5$: extremely contaminated

EF classes (Buat-Menard and Chesselet 1979): $EF < 2$: deficiency to minimal enrichment; $2 \leq EF < 5$: moderate enrichment; $5 \leq EF < 20$: significant enrichment; $20 \leq EF < 40$: very high enrichment; $EF \geq 40$: extremely high enrichment

C_f^i classes (Håkanson 1980): $C_f^i \leq 1$: low; $1 < C_f^i < 3$: moderate; $3 \leq C_f^i < 6$: considerable; $C_f^i \geq 6$: very high contamination

C_d classes (Håkanson 1980): $C_d < 8$: low; $8 \leq C_d < 16$: moderate; $16 \leq C_d < 32$: considerable; $32 \leq C_d < 80$: very high degree of contamination

mC_d classes (Abraham and Parker 2008): $mC_d < 1.5$: nil to very low; $1.5 \leq mC_d < 2$: low; $2 \leq mC_d < 4$: moderate; $4 \leq mC_d < 8$: high; $8 \leq mC_d < 16$: very high; $16 \leq mC_d < 32$: extremely high; $mC_d \geq 32$: ultra-high degree of contamination

PLI classes (Tomlinson et al. 1980): $PLI < 50$: drastic rectification measures are not needed; $PLI \geq 50-100$: detailed study and continuous monitoring required; $PLI \geq 100$: action needs to be taken

of the content causing 50 % inhibition, it cannot be excluded that significant though smaller adverse effects occur in these soils as well.

Conclusions

This study showed that the comparative investigation of soil properties and contaminant contents in topsoils and in small-scale depth gradients within topsoils from non-urban and urban soils is a suitable approach to reveal alterations in urban soils depending on anthropogenic impact intensity. The properties of soils in the region of Sulaimani city were clearly affected by urban activities. Although differences in single properties were largely nonsignificant, multivariate statistics using PCA revealed that combined alterations in contents of pedogenic oxides, carbonate, organic nitrogen and carbon as well as pH and CEC explained most of the dissimilarity of urban and non-urban soils. Contents of the investigated PTEs, Cd, Cu, Pb and Zn

were substantially higher in urban soils and increased with increasing anthropogenic soil use. The latter was well indicated by traffic volume and industrial use. Roadside soils are especially exposed to Pb contamination due to the ongoing use of Pb as fuel additive in Iraq. Higher contents within the ranges measured for the four PTEs in soils from roads and industrial areas even exceeded precautionary values. Mobility and transport of PTEs were small in the clayey, high-pH soils under a semiarid climate. On the other hand, this led to accumulation of PTEs, especially in the topmost centimeters of soil, thus particularly exposing humans to the contamination. Using assessment indices, contamination in roadside soils was classified as ‘moderate’ for Cu and Zn, and as ‘moderate’ to ‘considerable’ (contamination factor; C_f) for Cd and Pb. Contamination level was substantially lower, though, compared to many cities in industrialized countries. This is explained by a short accumulation time for pollutants in cities with a short history of industrialization and population growth such as Sulaimani. Nevertheless, both changes in general soil

properties and contamination may substantially impair soil functioning and ecosystem services. A toxicity index (*TI*) of 3.38 indicated that a toxic contamination level had been reached in some soils from the industrial areas and adverse effects on soil ecosystem functions must be expected. In total, it was found that the extent of alteration and contamination of urban soils in the area of Sulaimani city is still moderate. Even more, it appears timely and necessary to implement measures to reduce industrial emissions, especially to ban the use of leaded fuel. This will effectively lower soil contamination and safeguard the vulnerable semiarid environment.

Acknowledgments The help of Dr. H.K. Kamal; Prof. Dr. K.Z. Al Janabi and Mr. M. Qadir, University of Sulaimani, for soil sampling and of Mrs. P. Ziegler, Trier University, in the laboratory is highly acknowledged. M.S.H. Khorshid was financially supported by the Soil and Water Science, Faculty of Agriculture, University of Sulaimani, Kurdistan, Iraq.

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