



Phosphorus fractions and speciation in rural and urban calcareous soils in the semiarid region of Sulaimani city, Kurdistan, Iraq

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Received: 15 January 2019 / Accepted: 8 August 2019 / Published online: 17 August 2019
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Abstract

The phosphorus (P) status of soils depends, among other influencing factors such as soil properties, on P content and availability. These vary with the P distribution among species of different mobility and chemical behavior. The P distribution, in turn, depends on the parent rock material and pedoclimate, and may differ between land uses. This study assesses the impact of urbanization on P contents, fractions and speciation in rural versus urban soils in the region of Sulaimani city, Iraq. Topsoil samples from calcareous soils experiencing different human impact intensity were taken in and around Sulaimani city, spanning rural soils from near-natural grassland, riverbanks and arable land, and urban soils from city parks, roadsides and industrial areas. Changes in P status and speciation were determined by combining P fractionation through sequential chemical extraction and P K-edge XANES spectroscopy. The sequence of P contents in the different fractions was (percentage of total P extracted): citrate bicarbonate-P (0.9%) < NaOH-P (1.7%) < NaHCO₃-P (2.6%) ≤ citrate bicarbonate dithionate-P (3.8%) < residual P (36.2%) < HCl-P (54.8%). The dominance of stable Ca-phosphates (HCl-P) in all samples is typical for calcareous soils. The P distribution among fractions differed considerably in rural versus urban soils. Poor correlations of P fractions in urban soils with other soil parameters indicated that the P forms and contents were severely altered by human impact. P XANES analyses revealed that P speciation was dominated by P associated with Ca, especially in the urban area, and that irrigated arable land use increased the portions of P associated with pedogenic oxides. Soils of the semiarid regions in and around Sulaimani city exhibit a pattern of P fractions and species typical for calcareous soils. This pattern is clearly altered by human impacts such as agricultural land use and especially urban activities. It is concluded that the P inputs and turnover in urban soils are substantially decoupled from natural processes.

Keywords Rural soil · River soil · Urban soil · P fractionating extraction · XRD · XANES

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s12665-019-8543-2>) contains supplementary material, which is available to authorized users.

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Introduction

Phosphorus (P) is a primary essential nutrient element for plant growth and agricultural productivity; additionally, it may have significant negative environmental effects if

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present in the soil at high concentrations that exceed plant needs (Kruse et al. 2015; Ryan and Rashid 2006). Generally, P in soil is derived either by weathering of parent rock material, litter decay or from fertilizer inputs (Sharpley and Smith 1989; Sims and Vadas 2005). Within the soil, P mobilization via mineral weathering, P sorption/desorption and complexation as well as formation of secondary P minerals take place as a kinetic process. This results in the distribution of P among different P fractions and species that vary in mobility, bioavailability and chemical behavior (Ryan and Rashid 2006; Wang et al. 2010).

Information on these P species is highly relevant for plant nutrition and to assess the risk of P losses from soil, whereby P leaching into groundwater or adjacent surface water systems may cause subsequent eutrophication (Harrell and Wang 2006; Koch et al. 2018; von Wandruszka 2006). In calcareous soils, P is especially transformed into poorly available inorganic fractions that are mostly associated with Ca but encompass Al–P and Fe–P species as well (Beauchemin et al. 2003; Sims and Vadas 2005). Specific sequential P fractionation schemes have, therefore, been developed for calcareous soils to determine P fractions of different solubility and availability (Harrell and Wang 2006, 2007; Wang et al. 2010). Beyond these traditional wet chemical methods, more advanced and spectroscopic techniques such as ^{31}P -nuclear magnetic resonance spectroscopy or X-ray absorption near-edge structure (XANES) spectroscopy are also increasingly applied to identify P species (Beauchemin et al. 2003; Hedley et al. 1982; Kruse et al. 2015; Kuo 1996; Schlichting et al. 2002).

In general, human activities have multiplied the global turnover of P in the past decades (Smil 2000). A total movement of P from agricultural to urban ecosystems is typically found that results, e.g., from transport of agricultural goods to urban areas (Bittman et al. 2017). At the same time, the extent of urban land use is regarded as one of the major parameters strongly affecting total P loads in adjacent areas such as watersheds, for example due to dislocation of mobile P fractions (Meng et al. 2017; Tasdighi et al. 2017). Patterns of P distribution among different fractions and species can be affected by land uses (Jalali and Sajadi Tabar 2011). Therefore, information about the impact of land use on P species and transformations is fundamental to help avoid excessive P use and minimize environmental pollution. This calls for more research on this issue.

Sulaimani city is one of the largest cities in the autonomous semiarid region of Kurdistan in northeastern Iraq. The soilscape of the Sulaimani region is—based on earlier soil maps of Iraq (Buringh 1960)—separated into two main areas. The mountain valley is dominated by Kastanozems derived from weathering debris and erosion material along with associated Vertisols with high contents of expandable montmorillonite clays. Typically, areas with deeper soils

are used as arable land, where the traditional management is a 2-year dry farming/fallow cycle (Buringh 1960); alternatively, soils are irrigated (Zagonari 2017). The mountain area with its pronounced relief is mostly characterized by natural grassland with stony and shallow Rendzinas. Furthermore, Lithosols, Cambisols and Kastanozems are scattered in this area. More recent studies confirm the early work of Buringh (1960) and highlight the predominant impact of the parent material on the chemical composition of the calcareous, alkaline and mainly clayey soils (Abdulrazzaq 2004; Khorshid 2003; Rate and Sheikh-Abdullah 2017). Research on nutrient dynamics, including P in the soils of this region, is still needed.

Overall, information on the effects of different land uses on the P status of urban versus rural calcareous soils in semi-arid regions, and in particular on P speciation and different P fractions, is scarce. Therefore, the objectives of this study were (i) to determine the P status of calcareous soils within the semiarid region of Sulaimani city, (ii) to determine differences in the P status, distribution pattern among P fractions, and P speciation in urban versus rural soils, and (iii) to evaluate the relationships among P fractions and relevant soil properties. To this end, soils from areas in and around the city with different human impact intensity were investigated by applying a combination of sequential P fractionation as well as X-ray diffraction (XRD) and P K-edge X-ray absorption near-edge structure (XANES) spectroscopy.

Materials and methods

Study area and soil sampling

Soil samples were collected from Sulaimani city, Kurdistan Autonomous Region, Iraq, and its surrounding agricultural and near-natural areas (Fig. 1). Sulaimani city has 1.6 million inhabitants and is located at $35^{\circ}33'\text{N}$ and $45^{\circ}26'\text{E}$ in the Zagros Mountains at an altitude of about 860 m above sea level (Sulaimani Statistical Office 2014). The arid-summer Mediterranean climate (climate type 'Csa' according to Köppen–Geiger classification) is characterized by 600 mm mean annual precipitation and 18°C mean annual temperature. The Qiliansan stream flows west of Sulaimani city, joining the Tanjero River in the south. The downstream Tanjero River receives the city's effluents.

Soil samples were collected in March and April of 2010 and 2011. In total, 35 sites with different land use history were selected. The locations of all sampling points are shown in Fig. 1 and geographical information is provided in Table S1 (Supplementary material). Either four or five samples were taken from each of eight different soil use areas. Accordingly, sampling comprised four soils each from two of the most relevant arable land areas in the entire province,

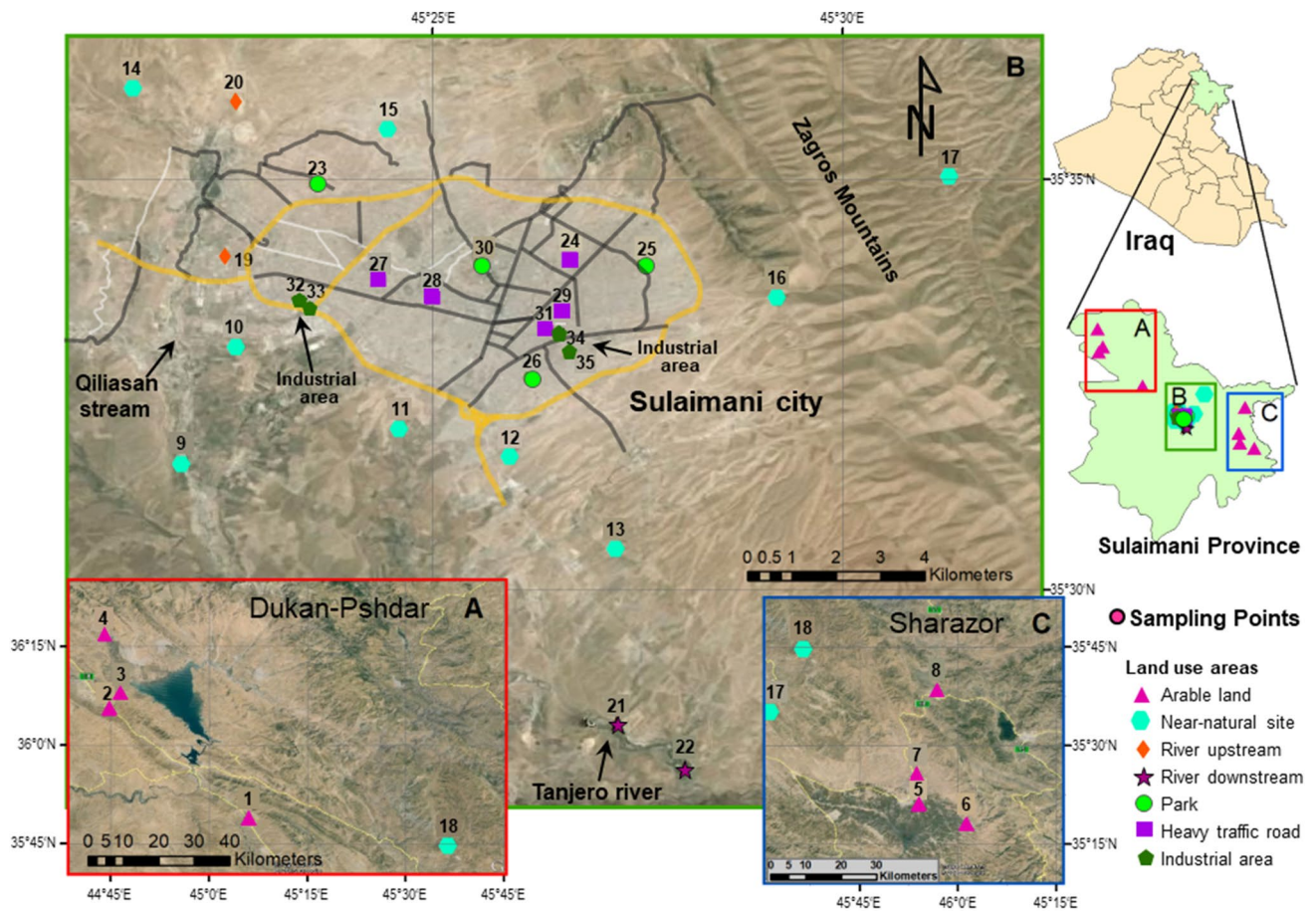


Fig. 1 Location of Sulaimani city within the Kurdistan Autonomous Region, Iraq; soil sampling sites in areas of different land use and anthropogenic impact (see Table S1 for sample identification by numbers)

i.e., Dukan–Pshdar (sample numbers 1–4) and Sharazor (5–8). Five soil samples were taken each from near-natural mountain areas in the south (9–13) and the north (14–18) of Sulaimani city that are characterized by extensively grazed grassland. Furthermore, four alluvial soils were sampled from river banks of the Qiliasan stream (19–20) upstream of Sulaimani city and of the Tanjero River (21–22) downstream of the city. For comparison, soils were sampled in urban areas of Sulaimani city, i.e., four in parks (23–26), five at roadsides of high-traffic roads (27–31) with a traffic volume of 1000–2000 vehicles h⁻¹, and four in industrial areas of the city (32–35), where business such as oil refineries, blacksmiths, car repair and paint shops are located.

Based on field observations and their chemical and physical properties, rural soils in the region were classified according to FAO guidelines (Jahn et al. 2006) as Rendzic Leptosols (thin mollic horizon above limestone shallower than 25 cm; near-natural soils), Leptic Kastanozems with mollic horizon thickness between 25 and 100 cm, and deep Vertic Kastanozems or Vertic Calcisols (arable soils) and Fluvisols (river soils).

Samples were taken from topsoil horizons, typically 0–10 cm depth for urban and grassland soils and 0–30 cm for arable soils. At each site, three individual samples were taken within 2 m distance and subsequently combined to one composite sample to reduce natural variations. The soils from the high-traffic areas were sampled within 1 m distance to the roadway, thereby ensuring that natural soil material and not technogenic material from road construction was sampled. All soil samples were air-dried and sieved to < 2 mm before further analyses.

Methods of soil analysis

General soil properties were determined following standard procedures (Blume et al. 2011; Soil Survey Staff 2014) and performed in duplicate if not indicated otherwise. Soil texture was determined following the FAO guidelines for soil description (Jahn et al. 2006) and the stone content (mineral particles > 2 mm) was analyzed gravimetrically. Soil pH was measured in soil suspension prepared at a soil:water ratio of 1:2.5 (w/w) using a glass electrode (pH/Cond 340i plus,

WTW, Weilheim, Germany). The potential cation exchange capacity (CEC) was determined after cation exchange with BaCl_2 buffered at pH 8.1 (Meiwes et al. 1984). Soil samples were extracted using ammonium oxalate to determine contents of the amorphous pedogenic oxides of iron (Fe), aluminum (Al) and manganese (Mn) (Schwertmann 1964). For this, the respective element contents in the extracts were determined by atomic absorption spectrometry (ContrAA 700 High-Resolution Continuum Source FI and/or AA-240 Graphite AAS, Varian, Darmstadt, Germany).

Total carbon (C) and nitrogen (N) were determined by gas chromatography after combustion at 1100 °C using a EuroEA elemental analyzer (HekaTech, Wegberg, Germany). Organic C (OC) and inorganic carbonate C (IC) were distinguished by carbonate removal as reported by Khorshid and Thiele-Bruhn (2016).

Total P was determined by acid digestion using pressure digestion vessels (DAB-2, Berghof, Eningen, Germany) following DIN EN 16174 (2012). Briefly, 0.2 g of soil was digested with 3 mL 65% HNO_3 and 1 mL H_2O_2 for 6 h at 150 °C. The P fractionation was done using separate samples and following the sequential extraction scheme proposed by Harrell and Wang (2007) for the determination of P fractions in calcareous soils. For this, 0.6 g of soil were sequentially extracted using five different extraction solutions and end-over-end shaking at 15 rpm under thermostated conditions (if not indicated otherwise).

According to Delgado and Torrent (2000) and Harrell and Wang (2006, 2007), the obtained five P fractions represent (1) NaHCO_3 -P: labile P including solution P, considered to be highly plant-available (hereafter ‘easily available’) and P bound to Fe and Al oxides. (2) NaOH -P: P adsorbed on mineral surfaces, released by the hydrolysis of Fe and Al phosphates, and by the hydrolysis of phosphated organic Fe and Al complexes. (3) Citrate bicarbonate-P (CB-P): P within labile pedogenic Ca-phosphates as well as P that was re-adsorbed to carbonate surfaces during the preceding NaOH -extraction. (4) Citrate bicarbonate dithionate-P (CBD-P): reductant-soluble P, mostly occluded in Fe oxides. (5) HCl -P: stable Ca-phosphates, including primary apatites. An additional sixth fraction, (6) the residual P-fraction, representing the chemically most stable inorganic and organic P forms, was calculated as the difference of the total amount of P and the sum of all five fractions from the P fractionation procedure. Further details on the procedure are provided in the Supplementary Material. Contents of total P as well as of P in sequential extraction fractions were determined by the molybdenum blue method (Murphy and Riley 1962) using a UV-Vis spectrophotometer at 710 nm (Shimadzu UV 1650-PC, Duisburg, Germany).

The XRD analyses were done on a subset of ten soil samples. Samples were selected to cover the different land uses as well as the different patterns of P fractions that

were obtained by principal component analysis (see section on statistical analysis) of the results of the sequential P extraction procedure. The X-ray diffraction (XRD) measurements were carried out with a Siemens XRD diffractometer D5000 (Siemens, Munich, Germany) using an incident angle between 2° and 35°, with a step size of $0.02^\circ \text{ s}^{-1}$, and using $\text{Co-K-}\alpha$ radiation (40 kV, 30 mA). The mineral content was semi-quantitatively determined using the software SIROQUANT Version 2.0 (CSIRO, Canberra, Australia).

Phosphorus K-edge XANES spectra were collected at the Soft X-ray Microcharacterization Beamline (SXRMB) at Canadian Light Source (CLS), Saskatoon, Canada. Due to beam time restrictions, a subset of five samples was selected from the sample set used for XRD analysis, representing the different land use types as well as the diverse mineral composition of the samples. To increase the P concentration and thus improve the signal-to-noise ratio of spectra, soil samples were first preprocessed by particle size fractionation to remove the sand fraction and separate the silt and clay fractions that are known to be enriched in P and organic matter. For this, samples were physically dispersed in distilled water by ultrasonic treatment according to Leinweber (1995), Amelung et al. (1998), and Schmidt et al. (1999) using an ultrasonic bath (Sonorex Super RK 514 BH, Bandelin, Berlin, Germany). Subsequently, the sand fraction was removed by wet sieving through a 63- μm mesh screen. The remaining fine particle size fraction was centrifuged at $5000\times g$, freeze-dried and homogenized. For P XANES measurements, size-fractionated soil samples were spread as a thin film onto a double-sided carbon tape and mounted onto a copper sample holder before placement in the vacuum chamber. The spectra were recorded in fluorescence yield mode (samples) and total electron yield mode (reference standards), respectively, at photon energies between 2115 and 2205 eV. For each sample, at least two scans were recorded. Subsequent data treatment and evaluation such as spectra averaging, background correction and normalization as well as linear combination fitting were done using the ATHENA software package (Demeter 0.9.24) (Ravel and Newville 2005). Linear combination fitting was performed on averaged, normalized spectra in the energy range between -10 and $+31$ eV, relative to the E_0 . Fitting was done for all possible binary to quaternary combinations of the 15 most probable P reference standards in the sample: CaHPO_4 , $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{H}_2\text{PO}_4)_2\cdot \text{H}_2\text{O}$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, AlPO_4 , $\text{FePO}_4\cdot 4\text{H}_2\text{O}$, P adsorbed on gibbsite, P adsorbed on iron goethite, $\text{Mg}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$, $\text{Mg}_2\text{O}_7\text{P}_2$, $\text{MgHPO}_4\cdot 3\text{H}_2\text{O}$, KH_2PO_4 , K_3PO_4 , $(\text{NH}_4)_2\text{HPO}_4$, $\text{K}_4\text{P}_2\text{O}_7$ and phytic acid sodium salt hydrate ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6\cdot x\text{Na}^+\cdot y\text{H}_2\text{O}$). The residual factor (R factor) values were used as goodness-of-fit criteria.

Statistical analysis

Statistical analysis, including descriptive statistics and Pearson correlation analysis, was carried out using the IBM SPSS Statistics 23 software (IBM, New York, USA). The non-parametric Mann–Whitney U test was used to determine significant differences between groups at $p \leq 0.05$. Principal component analysis was performed using the oblimin direct rotation to determine differences in patterns of P fractions among samples and land uses.

Results

Basic soil properties

Information on general properties of the investigated soils is given in Table 1 and more detailed data in Table S2 (Supplementary Material). The texture of all 35 soils ranged between silty clay loam and sandy loam with a slight trend towards coarser textures in urban soils. The corresponding clay contents ranged from 7.9 to 53% (mean arable and near-natural soils 33.4%, mean urban soils 26.6%). The stone content (> 2 mm) was on average much higher in urban compared to near-natural and arable soils (mean arable and near-natural soils 8.9%, mean urban soils 58.6%). Among all the different rural land uses, the average OC content in the soils did not exceed 17 g C kg^{-1} . In contrast, OC contents were significantly higher in soils from the industrial areas (mean 40 g C kg^{-1}). This was accompanied by significantly higher mean C/N ratios of 21.7 in the soils from the industrial areas compared to all other soils, indicating differences in the soil organic matter composition (Table 1).

The contents of amorphous pedogenic Al and Mn oxides were mostly significantly larger in rural versus urban soils (Table 1). However, the differences in the Fe_{ox} contents were not statistically significant between most of the rural and urban soil use groups, which was due to the much higher variability in the Fe_{ox} contents in urban soils. Highest Fe_{ox} contents were recorded in several soils from the industrial areas and the soils from the river banks downstream of the city (Table 1).

Soils from all sampling sites were characterized by weakly alkaline $\text{pH}_{\text{H}_2\text{O}}$ values (7.5–7.9) along with high IC contents in a range from 3 to 55 g C kg^{-1} (Table 1). The presence of carbonates was further confirmed by XRD analysis of ten representative samples (Table 2). Calcite was the dominant mineral in all samples, whereas dolomite was present only in the two arable soil samples. The IC contents differed significantly between land uses, with highest contents in soils from river banks and all urban soils. Apart from carbonates, the mineral composition of the soils was dominated by illite and partly by mica and feldspar (albite) (Table 2).

In comparison, much smaller amounts of the more intensely weathered kaolinite and chlorite clay minerals were found in the samples. All samples also contained smectite, but it was especially prominent in two samples from a near-natural grassland and one arable site. By contrast, gypsum was identified only in one sample from an industrial site.

Total P contents and P fractions

The total P content varied in all 35 soil samples between 366 and 1260 mg kg^{-1} (Table 3; more detailed data are given in Table S3 in the Supplementary Material). The total P contents in the soils under the different land use followed the order arable soils (Dukan–Pshdar) $<$ arable soils (Sharazor) $<$ urban industrial areas $<$ near-natural area (Sulaimani south) $<$ urban parks $<$ river bank soils $<$ urban roadsides $<$ near-natural area (Sulaimani north) (Table 3). The only significant differences, however, were between arable soils (Dukan–Pshdar) and roadside soils. Among the different fractions, the highest P contents occurred in the HCl-P and residual-P fraction, accounting on average for 55 and 36% of the total P, respectively (Table 3). By contrast, the other four fractions together only accounted on average for $< 9\%$ of total P.

The P portions in the first four fractions of the sequential extraction scheme differed between arable soils and soils of other land uses (Fig. 2a–d). While labile NaHCO_3 -P tended to be lowest in the arable soils, P contents in the NaOH, CB and CBD fractions were substantially and, in most cases, significantly larger in arable soils compared to other land uses. In contrast, among all land uses, urban soils showed the highest NaHCO_3 -P contents, whereas P contents were low in the other three fractions (NaOH-P, CB-P, CBD-P). Note, however, that among urban soils, the differences between land use types, i.e., soils from parks, roadsides, and industrial areas, were negligible. The proportions of HCl-P and residual P on total P were lowest and highest, respectively, in urban soils, while the opposite was found for the arable soils (Fig. 2e, f). In general, proportions of HCl-P and residual P in soils from near-natural areas and river bank soils were between the two extremes marked by the arable and urban soils. At the same time, the proportions of NaOH-P, CB-P and CBD-P on total P in near-natural soils were more similar to urban and river bank soils than to arable soils (Fig. 2b–d). The river banks were sampled from areas upstream and downstream of Sulaimani city to examine a possible urban impact. The river bank soils from these two locations differed substantially. The proportions and contents of easily available NaHCO_3 -P at the downstream river bank sites were the highest of all soils. Upstream and downstream differences in P fractions were also observed for NaOH-P, CB-P, HCl-P, residual P (Fig. 2b–e; Table 3) and total P (607 mg kg^{-1} in upstream soils and 806 mg kg^{-1} in

Table 1 Properties of 35 topsoil samples from sites of different land use in and around Sulaimani city

| | <i>n</i> | pH _{H2O} | CEC (cmol _c kg ⁻¹) | IC (%) | OC (%) | C/N | Fe _{ox} (g kg ⁻¹) | Al _{ox} (g kg ⁻¹) | Mn _{ox} (g kg ⁻¹) | Clay ^A (%) | Stones ^B (%) |
|--------------------|----------|-------------------|---|-------------------|--------------------|--------------------|--|--|--|-----------------------|-------------------------|
| Arable land | | | | | | | | | | | |
| Dukan-Pshdar | Mean | 7.6 ^{bc} | 31.7 ^b | 2.2 ^{bc} | 1.2 ^c | 6.7 ^{abc} | 0.9 ^a | 1.7 ^c | 0.4 ^{bc} | 30.2 ^c | 4.7 ^a |
| | Stdev. | 0.1 | 1.9 | 1.3 | 0.2 | 6.0 | 0.1 | 0.3 | 0.1 | 2.2 | 2.8 |
| Sharazor | Mean | 7.4 ^a | 20.0 ^a | 0.6 ^a | 1.2 ^{bc} | 4.4 ^a | 0.9 ^a | 1.3 ^b | 0.3 ^b | 20.4 ^{ab} | 3.8 ^a |
| | Stdev. | 0.1 | 2.8 | 0.3 | 0.4 | 1.0 | 0.3 | 0.2 | 0.0 | 4.6 | 2.4 |
| Near-natural areas | | | | | | | | | | | |
| Sulaimani south | Mean | 7.7 ^c | 41.2 ^c | 3.0 ^c | 0.8 ^b | 6.7 ^b | 1.4 ^{bc} | 1.5 ^{bc} | 0.5 ^c | 39.5 ^d | 3.0 ^a |
| | Stdev. | 0.1 | 4.8 | 0.7 | 0.3 | 0.7 | 0.4 | 0.6 | 0.1 | 2.1 | 1.6 |
| Sulaimani north | Mean | 7.5 ^b | 40.1 ^c | 1.6 ^{ab} | 1.7 ^d | 7.3 ^{bc} | 1.6 ^c | 1.9 ^{bc} | 0.8 ^d | 40.1 ^d | 22.1 ^b |
| | Stdev. | 0.1 | 10.2 | 1.0 | 0.6 | 2.8 | 0.4 | 0.2 | 0.2 | 12.6 | 7.6 |
| River banks | | | | | | | | | | | |
| All samples | Mean | 7.7 ^c | 29.3 ^b | 4.8 ^d | 0.5 ^a | 9.2 ^{bc} | 1.6 ^{abc} | 0.8 ^a | 0.2 ^a | 30.1 ^c | 91.8 ^d |
| | Stdev. | 0.1 | 2.7 | 1.2 | 0.1 | 2.2 | 0.8 | 0.3 | 0.1 | 3.3 | 8.8 |
| Upstream | Mean | 7.8 | 30.3 | 4.0 | 0.5 | 7.6 | 1.0 | 0.6 | 0.3 | 31.5 | 86.6 |
| | Mean | 7.7 | 28.2 | 5.6 | 0.6 | 10.8 | 2.3 | 1.0 | 0.2 | 28.8 | 97.0 |
| Urban areas | | | | | | | | | | | |
| Parks | Mean | 7.8 ^c | 35.2 ^{cb} | 4.4 ^d | 1.4 ^{bcd} | 7.0 ^b | 0.7 ^a | 0.8 ^a | 0.3 ^{ab} | 33.6 ^{cd} | 51.8 ^c |
| | Stdev. | 0.1 | 8.4 | 0.4 | 0.8 | 1.1 | 0.4 | 0.2 | 0.1 | 11.9 | 46.2 |
| Roadsides | Mean | 7.7 ^{bc} | 31.5 ^{bc} | 4.5 ^d | 1.3 ^{cd} | 9.0 ^c | 1.3 ^b | 0.9 ^a | 0.2 ^{ab} | 29.6 ^{ab} | 80.3 ^d |
| | Stdev. | 0.2 | 8.5 | 0.6 | 0.4 | 3.2 | 0.6 | 0.2 | 0.1 | 10.4 | 26.7 |
| Industrial areas | Mean | 7.6 ^b | 23.2 ^{ab} | 4.9 ^d | 4.0 ^e | 21.7 ^d | 2.0 ^{abc} | 0.9 ^a | 0.3 ^{ab} | 15.9 ^a | 38.4 ^{bc} |
| | Stdev. | 0.1 | 10.9 | 0.4 | 1.5 | 8.8 | 1.3 | 0.2 | 0.1 | 13.5 | 35.2 |

Mean and standard deviation of data of soil pH, cation exchange capacity (CEC), inorganic, carbonate carbon (IC), organic carbon (OC), carbon to nitrogen ratio of organic matter (C/N), and oxalate-extractable iron, aluminum and manganese (Fe_{ox}, Al_{ox}, Mn_{ox})

n sample count

^A Average (minimum–maximum) content of clay in fine earth < 2 mm

^B Average percentage of stones > 2 mm in whole soil sample

^C Similar letters indicate statistical similarity of means ($p \leq 0.05$); comparison within individual soil parameters

Table 2 Dominating minerals in selected soil samples of different land use as identified by X-ray diffraction (XRD) analysis; semi-quantitative determination as percentage of total signal area

| No. ^a | Land use and site | Quartz | Albite | Calcite | Dolomite | Pyrite | Gypsum | Illite + mica | Smectite | Chlorite | Kaolinite |
|------------------|---------------------------|--------|--------|---------|----------|--------|--------|---------------|----------|----------|-----------|
| 2 | Arable Dukan-Pshdar | 20 | n.d. | 66 | 1 | n.d. | n.d. | 7 | 1 | 2 | 3 |
| 5 | Arable Sharazor | 26 | n.d. | 22 | 8 | n.d. | n.d. | 21 | 3 | 11 | 9 |
| 11 | Near-natural Sulai. south | 32 | 6 | 39 | n.d. | n.d. | n.d. | 11 | 1 | 5 | 6 |
| 13 | Near-natural Sulai. south | 18 | 7 | 47 | n.d. | n.d. | n.d. | 22 | 6 | n.d. | n.d. |
| 17 | Near-natural Sulai. north | 43 | 5 | 14 | n.d. | 2 | n.d. | 19 | 1 | 7 | 9 |
| 19 | Riverbank upstream | 11 | 4 | 16 | n.d. | n.d. | n.d. | 53 | 1 | n.d. | 15 |
| 23 | Urban park | 30 | 2 | 48 | n.d. | n.d. | n.d. | 9 | 1 | 4 | 6 |
| 27 | Urban roadside | 26 | 4 | 43 | n.d. | n.d. | n.d. | 16 | 1 | 5 | 5 |
| 30 | Urban roadside | 27 | 4 | 44 | n.d. | n.d. | n.d. | 13 | 1 | 5 | 6 |
| 35 | Urban industrial area | 29 | 6 | 39 | n.d. | n.d. | 6 | 11 | 1 | 3 | 5 |

n.d. not detectable

^aSample numbers correspond to the numbers in Table 5 and Table S1

Table 3 Phosphorus contents in sequential extracts from 35 topsoil samples from sites of different land use in and around Sulaimani city

| | <i>n</i> | | NaHCO ₃ -P | NaOH-P | CB-P | CBD-P | HCl-P | Residual P | Total P |
|--------------------|----------|------------|-----------------------|---------------------|--------------------|---------------------|----------------------|---------------------|---------------------|
| Arable land | | | | | | | | | |
| Dukan–Pshdar | 4 | Mean | 3.44 ^{abA} | 17.64 ^{bc} | 10.84 ^c | 35.65 ^b | 312.5 ^{abc} | 81.47 ^a | 461.5 ^a |
| | | Stdev. | 1.75 | 17.16 | 1.06 | 22.58 | 111.9 | 46.10 | 80.43 |
| Sharazor | 4 | Mean | 4.38 ^a | 29.14 ^c | 13.51 ^c | 66.99 ^c | 266.5 ^{ab} | 109.2 ^{ab} | 489.7 ^{ab} |
| | | Stdev. | 1.72 | 11.68 | 7.43 | 18.68 | 92.81 | 103.0 | 203.1 |
| Near-natural areas | | | | | | | | | |
| Sulaimani south | 5 | Mean | 13.44 ^{ab} | 6.79 ^{ab} | 1.29 ^a | 17.74 ^{ab} | 394.1 ^{bc} | 185.5 ^b | 618.9 ^{ab} |
| | | Stdev. | 14.89 | 4.80 | 0.77 | 12.59 | 92.54 | 110.8 | 59.40 |
| Sulaimani north | 5 | Mean | 12.98 ^a | 5.76 ^{ab} | 2.44 ^{ab} | 17.40 ^{ab} | 454.6 ^{bc} | 349.9 ^{bc} | 843.0 ^b |
| | | Stdev. | 6.76 | 5.23 | 2.48 | 15.36 | 180.5 | 284.6 | 357.6 |
| River banks | | | | | | | | | |
| All samples | 4 | Mean | 36.14 ^b | 4.97 ^{ab} | 2.22 ^{ab} | 4.90 ^a | 425.8 ^c | 232.6 ^b | 706.6 ^{ab} |
| | | Stdev. | 27.59 | 4.58 | 1.30 | 1.19 | 43.54 | 54.62 | 120.4 |
| Upstream | 2 | Mean | 14.92 | 1.38 | 1.28 | 4.17 | 398.2 | 187.3 | 607.2 |
| | | Downstream | 2 | Mean | 57.36 | 8.55 | 3.17 | 5.63 | 453.3 |
| Urban areas | | | | | | | | | |
| Parks | 4 | Mean | 26.42 ^b | 1.74 ^a | 3.07 ^{ab} | 5.43 ^a | 301.7 ^{abc} | 339.5 ^{bc} | 677.9 ^{ab} |
| | | Stdev. | 26.62 | 1.54 | 2.18 | 3.06 | 157.7 | 81.42 | 263.4 |
| Roadsides | 5 | Mean | 31.34 ^b | 2.32 ^a | 4.11 ^a | 6.56 ^a | 368.4 ^{bc} | 339.5 ^{bc} | 752.2 ^b |
| | | Stdev. | 17.36 | 1.28 | 2.57 | 3.39 | 88.08 | 219.3 | 317.4 |
| Industrial areas | 4 | Mean | 23.60 ^b | 2.73 ^a | 2.77 ^{ab} | 5.13 ^a | 216.1 ^a | 347.0 ^c | 597.3 ^{ab} |
| | | Stdev. | 17.94 | 1.04 | 1.32 | 1.22 | 65.91 | 65.61 | 136.04 |

Number of samples (*n*); mean (mg kg⁻¹) and standard deviation (stdev.) of data

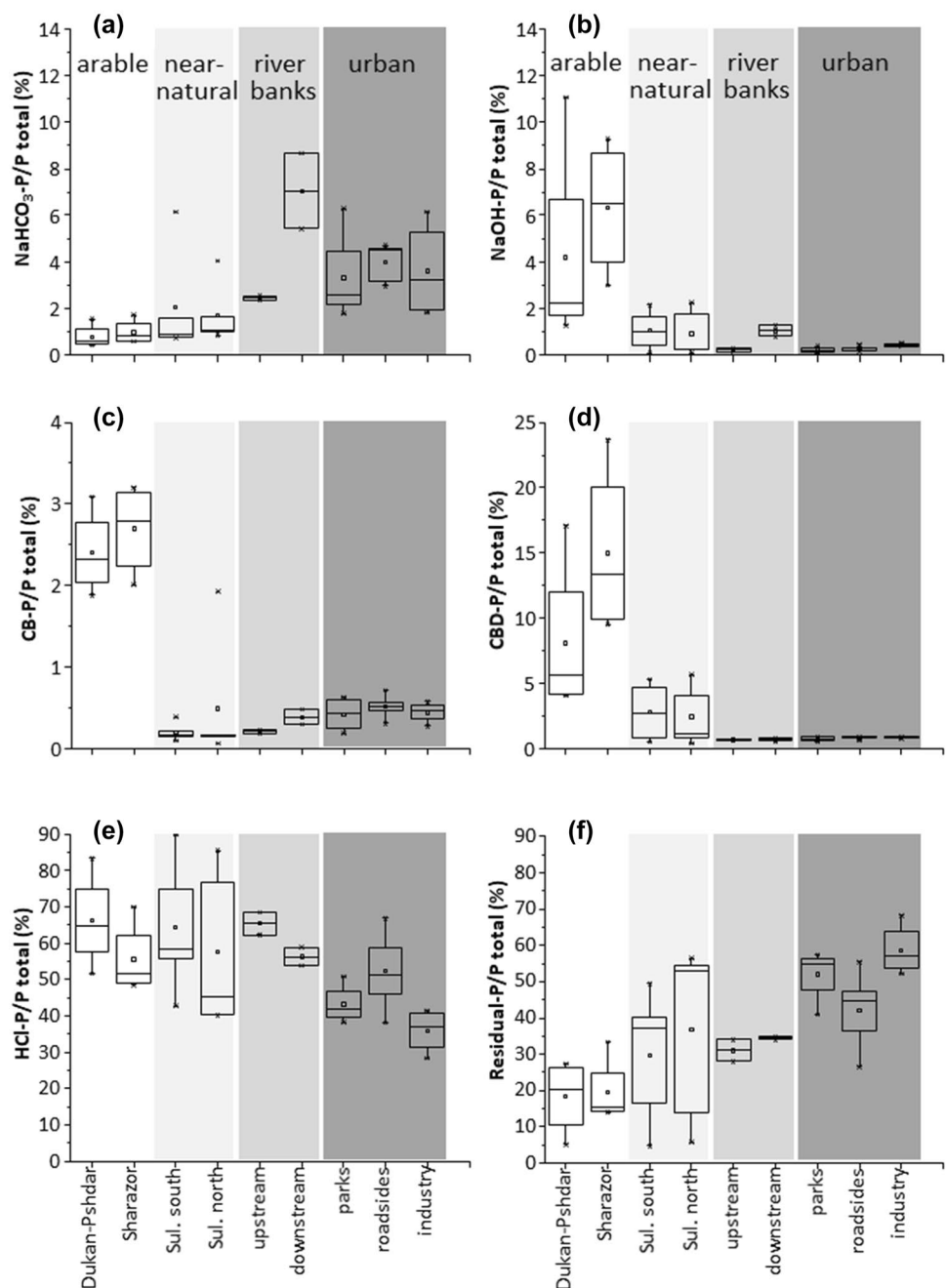
^ADifferent letters indicate statistically significant difference of means ($p \leq 0.05$); comparison within the individual P fractions

downstream soils). Note, however, that the small number of river bank soil samples required the statistical evaluation to be done for all four samples (without upstream/downstream distinction).

Data from sequential P fractionation were further evaluated by PCA. The results indicated a land use-induced

pattern in the distribution of P among the different fractions (Fig. 3). About 83% of the variance was explained by the first two principle components (PC). Urban and arable soils were located in clearly different clusters along PC1. A further sub-clustering along PC2 was indicated for the urban soils. Soils from the near-natural areas clustered along PC1

Fig. 2 Proportions of P from total P in five sequential extraction fractions (Harrell and Wang 2007) plus a residual fraction from soils of different land use at rural and urban sites in and around Sulaimani city, **a** $\text{NaHCO}_3\text{-P}$, **b** NaOH-P , **c** CB-P , **d** CBD-P , **e** HCl-P , **f** residual P. Boxes mark the 25% and 75% percentile with median (line) and arithmetic mean (square) inside; whiskers show 1.5–98.5% percentile and stars extreme values (1 and 99% percentile)



between the arable and urban soils with distinct overlaps with the latter, whereas on PC2 only half of the samples were separated from the urban soils. Figure 3 shows that the separation between areas of different land uses depended on CB-P , NaOH-P , and CB-P . This is because these fractions loaded most and quite similarly on PC1, whereas HCl-P and residual-P loaded with opposing effect on PC2.

The P contents in the different extraction fractions correlated in part with each other and with different soil properties. Importantly, these correlations were very different between the rural and urban sites (Table 4). Whereas in the

urban soils the P contents of most fractions and of total P were significantly correlated ($p \leq 0.05$), this applied much less to P fractions of rural soils. This coincides with the close similarity of the P fraction patterns in urban soils and the much wider scattering of data points from rural soils determined by PCA (Fig. 3). A similar discrepancy between urban and rural soils was found for the correlations between total P and P in fractions with other soil parameters. For rural soils, significant and in part very close, positive correlations were found for the easily extractable fractions NaOH-P , CB-P and CBD-P with Fe_{ox} and Mn_{ox} . For $\text{NaHCO}_3\text{-P}$;

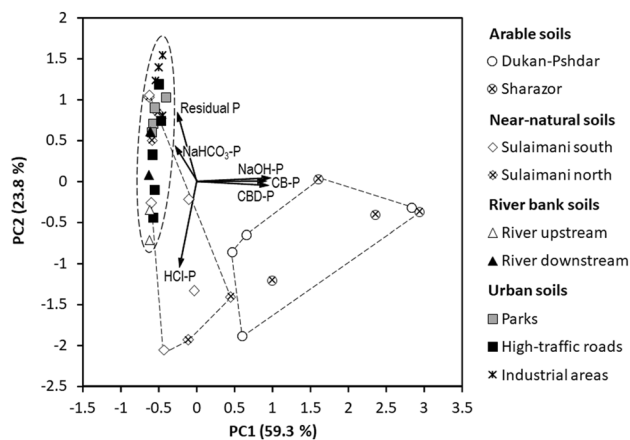


Fig. 3 Principal component analysis of relative portions of P in five sequential-extraction fractions and a residual fraction of rural and urban soils from the Sulaimani region. Broken lines indicate the boundaries within which arable soils and soils from near-natural grassland sites, respectively, cluster, while all other samples cluster within the oval ring. Factor loadings are indicated by labelled arrows

however, these correlations were negative (Table 4). Residual P correlated with OC. In contrast, only few correlations, with a low significance level, were determined for urban soils.

P minerals and species

Although all samples contained large proportions of HCl-P, which primarily represents P associated with Ca, XRD analyses were unable to identify any P-containing mineral phases (Table 2). Hence, we applied more sensitive element-specific P K-edge XANES analysis on selected samples representing four different land use types. LC-fitting revealed that P was present in different mineral species, with Ca-associated P in the form of apatite always being the main P phase in all samples (Table 5). Here, lower proportions were measured in the rural soils (especially for near-natural soils from the north) and higher proportions in the urban soils. The proportions of organic P species were generally too low in all samples to be detectable. Iron-associated P was present in all samples, while clear differences were evident in the P species that occurred in smaller quantities. FePO_4 and $\text{K}_4\text{P}_2\text{O}_7$ were found only in rural samples, while $\text{Ca}(\text{H}_2\text{PO}_4)_2$ was detected only in one of the urban soil samples (Table 5).

Discussion

Soils of the Sulaimani region are all strongly to extremely calcareous according to the FAO classification (Jahn et al. 2006). The high carbonate contents mostly originate from the widespread calcitic and dolomitic parent rock material

(Rate and Sheikh-Abdullah 2017; Yousefifard et al. 2012). The overall pattern of dominant soil minerals points to an intermediate to young state of soil development (Jackson and Sherman 1953). This is typical for soils in semiarid regions with marked water deficits (Schoonejans et al. 2016), while the observed further increases in coarse material and carbonate contents are typical features of urban soils (Asabere et al. 2018). More detailed information about additional basic properties of the soils in the region of Sulaimani city and their alteration due to urbanization was reported by Khorshid and Thiele-Bruhn (2016).

This study focused on the P status in calcareous soils and effects of land use on the P contents and P distribution. In all investigated soils of the semiarid region of Sulaimani city, stable Ca-phosphates (HCl-P) largely dominated the inorganic P species, which agrees with previous studies (Jalali and Sajadi Tabar 2011). Contents of HCl-P were larger by factors of 30–50 than the easily available, metal oxide-bound, and occluded phosphate fractions (Fig. 2; Table 3). A similar prevalence of HCl-P was found in other calcareous soils and river sediments in semiarid as well as temperate regions (Delgado and Torrent 2000; Harrell and Wang 2006; Jalali 2010; Saavedra and Delgado 2005). In contrast, in acidic (non-calcareous) soils, P associated with Al and Fe oxyhydroxides dominates (Carreira et al. 2006; Delgado and Torrent 2000).

Accordingly, P XANES analysis revealed that P bound in apatite was the dominating P species in rural and urban soils. In general, the relative abundance of P species and of matching P fractions agreed well. Nonetheless, P XANES analysis revealed somewhat higher contents of apatite in urban soil samples, probably reflecting a larger share of lithogenic resources in these soils, as was deduced from their higher stone content (Khorshid and Thiele-Bruhn 2016). It could not be clarified, though, whether the detected Ca-phosphates represented lithogenic, primary apatite or pedogenic minerals such as secondary apatite or octocalcium phosphate.

In the area of Sulaimani city, soil total P tended to be higher in urban and adjacent river soils compared to arable soils, but it was similarly high in near-natural grassland soils. Similar results were reported by Plak et al. (2017), who found high P contents in urban Technosols but even higher total P contents in rural, near-natural soils. The observed total P contents in urban soils ranged from 0.4 to 1.2 g kg^{-1} and were within the range of 0.96–2.5 g kg^{-1} reported for other major cities in China, Romania and the UK (Lacatusu et al. 2008; Li et al. 2018; Meng et al. 2017; Yuan et al. 2007; Zhang and Ke 2004). Li et al. (2018) and Zhang (2004) reported clear relationships between the degree of urbanization and total P content in soils, with gradients from urban to suburban and rural soils. However, no such clear relationships between urbanization and total P

Table 4 Coefficients of Pearson correlation of phosphorus (P) contents in fractions obtained by a sequential extraction scheme and total P with selected soil parameters from rural (arable, near-natural, river soil upstream, $n=20$) and urban sites (river soils downstream, parks, roadsides, industrial areas) ($n=15$)

| | NaOH-P | CB-P | CBD-P | HCl-P | Residual P | Total P | pH | CEC | OC | IC | C/N | Fe _{ox} | Al _{ox} | Mn _{ox} | Clay |
|-----------------------|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|----------|----------------|---------------|----------|----------------|------------------|------------------|------------------|--------|
| Rural soils | | | | | | | | | | | | | | | |
| NaHCO ₃ -P | -0.370 | -0.402 | -0.445* | 0.040 | 0.359 | -0.029 | 0.102 | 0.416 | 0.179 | 0.292 | -0.179 | -0.430 | -0.153 | -0.463* | -0.056 |
| NaOH-P | <i>0.746***</i> | <i>0.927***</i> | -0.338 | -0.338 | -0.318 | -0.063 | -0.677** | -0.493* | 0.124 | -0.597** | <i>0.558**</i> | <i>0.459*</i> | 0.298 | <i>0.722***</i> | 0.287 |
| CB-P | | <i>0.713***</i> | -0.374 | -0.297 | -0.297 | -0.159 | -0.589** | -0.700** | 0.262 | -0.376 | <i>0.551*</i> | <i>0.637**</i> | 0.245 | <i>0.744***</i> | 0.241 |
| CBD-P | | | -0.231 | -0.285 | -0.285 | 0.050 | -0.675** | -0.474* | 0.121 | -0.666** | <i>0.476*</i> | <i>0.477*</i> | 0.364 | <i>0.825***</i> | 0.370 |
| HCl-P | | | | 0.704 | 0.704 | 0.957 | 0.152 | <i>0.569**</i> | 0.131 | -0.046 | -0.338 | -0.321 | 0.193 | -0.363 | -0.048 |
| Residual P | | | | 0.664 | 0.664 | 0.664 | 0.059 | <i>0.553*</i> | <i>0.544*</i> | -0.172 | -0.230 | -0.193 | 0.351 | -0.270 | -0.020 |
| Total P | | | | | | | -0.062 | <i>0.452*</i> | 0.200 | -0.237 | -0.192 | -0.199 | 0.305 | -0.145 | 0.015 |
| Urban soils | | | | | | | | | | | | | | | |
| NaHCO ₃ -P | <i>0.823***</i> | <i>0.752**</i> | <i>0.771**</i> | <i>0.874***</i> | <i>0.854***</i> | <i>0.914***</i> | 0.100 | 0.357 | -0.383 | -0.126 | -0.178 | 0.047 | 0.353 | -0.537* | -0.111 |
| NaOH-P | 0.375 | 0.398 | 0.629* | 0.518* | 0.518* | 0.676** | -0.072 | -0.030 | -0.240 | 0.295 | -0.380 | 0.329 | 0.457 | -0.407 | -0.491 |
| CB-P | | <i>0.965***</i> | <i>0.714**</i> | <i>0.893***</i> | <i>0.893***</i> | <i>0.743**</i> | -0.016 | 0.317 | -0.156 | -0.341 | 0.307 | 0.011 | 0.477 | -0.242 | 0.168 |
| CBD-P | | | <i>0.720**</i> | <i>0.931***</i> | <i>0.931***</i> | <i>0.751**</i> | 0.003 | 0.301 | -0.143 | -0.39 | 0.234 | 0.075 | 0.353 | -0.227 | 0.087 |
| HCl-P | | | | <i>0.836***</i> | <i>0.836***</i> | <i>0.996***</i> | 0.112 | 0.437 | -0.589* | -0.142 | -0.232 | 0.015 | 0.267 | -0.528* | 0.099 |
| Residual P | | | | <i>0.860***</i> | <i>0.860***</i> | <i>0.860***</i> | 0.167 | 0.471 | -0.320 | -0.353 | 0.038 | 0.013 | 0.353 | -0.327 | 0.145 |
| Total P | | | | | | | 0.107 | 0.426 | -0.556* | -0.142 | -0.219 | 0.027 | 0.295 | -0.534* | 0.119 |

Significant correlations are indicated by table cells with italics and indication of the following level of significance (p): *** ≤ 0.001 ; ** ≤ 0.01 ; * ≤ 0.05 , no symbol ≤ 0.1

Table 5 Major P species in selected soil samples of different land use; quantification as percentage of total signal area (identification and determination by P K-edge XANES analyses)

| No. ^a | Land use and site | K ₄ P ₂ O ₇ | Mg ₂ O ₇ P ₂ | Apatite | Ca(H ₂ PO ₄) ₂ ·H ₂ O | P sorbed on FeOOH | FePO ₄ ·4H ₂ O | R factor |
|------------------|---------------------------|--|---|---------|--|-------------------|--------------------------------------|----------|
| 2 | Arable Dukan–Pshdar | 10.2 | 2.4 | 64.0 | | 15.2 | 8.3 | 0.00218 |
| 11 | Near-natural Sulai. south | 6.0 | 7.7 | 66.0 | | 14.8 | 5.6 | 0.00312 |
| 17 | Near-natural Sulai. north | 1.8 | 19.1 | 55.7 | | 19.8 | 3.6 | 0.00106 |
| 30 | Urban roadside | | 5.6 | 73.6 | 5.1 | 15.7 | | 0.00191 |
| 35 | Urban industrial area | | 10.8 | 73.5 | | 15.7 | | 0.00389 |

^aSample numbers correspond to the numbers in Table 2 and Table S1

contents could be confirmed in this and other studies (Yuan et al. 2007).

The effect of different land uses on P status was much better indicated by differences in the P distribution pattern over fractions of different P solubility and availability obtained from the sequential P extraction. In general, the distribution of P among the extraction fractions corresponded to previous reports for urban soils (e.g., Zhang 2004) and arable soils (Harrell and Wang 2006). Higher proportions and concentrations of labile and easily available P in soils from urban parks versus rural soils corresponded with findings on soils from urban compared to rural forests (Hu et al. 2011). In urban soils (parks, roadsides, industrial areas) in Sulaimani city, the average content of NaHCO₃-P was 27.1 mg kg⁻¹. Since the extraction procedure for NaHCO₃-P is identical to the Olsen-P extraction, this result can be related to the general threshold value for P leaching of 25 mg kg⁻¹ Olsen-P that was proposed by Zhang et al. (2005) and Hu et al. (2011) based on data from numerous soils of different urban areas. The exceeding of the threshold indicates that urban soils, even when they are calcareous, can be a significant source of P losses to aquatic environments. In Sulaimani that may occur during the rainy winter season from November to April. Note, however, that a general threshold can only be a rough indicator; exact thresholds must be adjusted for specific soil properties.

The reported differentiation between soils with different urbanization histories—with stronger changes in P forms at older urban sites (Scharenbroch et al. 2005; Yesilonis et al. 2016; Yuan et al. 2007)—was not confirmed here. No substantial differences were found in the contents and distribution of P forms in soils with different urban land use histories. This is explained by the rather short, recent history of population growth and industrialization in Sulaimani city, which was founded in 1784 (Khorshid and Thiele-Bruhn 2016). Importantly, many significant correlations of individual P fractions with other soil parameters were found for rural soils, but much less so for urban soils. This indicates that P forms and contents in urban soils were seriously altered or even replaced by human activity. The few

correlations determined did not match with the definitions of the P fractions, e.g., relating P to soil organic matter, and pedogenic oxides (Delgado and Torrent 2000; Harrell and Wang 2007). For example, the contents of Fe_{ox} in urban soils and of NaOH-P and CBD-P were not correlated, although the two P fractions are defined to represent “P adsorbed on mineral surfaces, released by the hydrolysis of Fe and Al phosphates, and by the hydrolysis of phosphated organic Fe and Al complexes” and “P occluded in Fe oxides”, respectively (Harrell and Wang 2007; for definitions of other P fractions see “Materials and methods”). Furthermore, correlation and multivariate statistics showed that the P distribution among fractions was very similar in urban but dissimilar in rural soils (Fig. 3, Table 4). This suggests that urban land uses alter P speciation towards a more uniform pattern, with higher labile and higher residual fractions and a decoupling of the P distribution among the different fractions from natural pedogenesis. Known anthropogenic inputs that enrich the labile P fraction (NaHCO₃-P) are fertilizer use in parks and private gardens, animal excreta and human wastes, dust from motor traffic and especially from wear of brake linings (Bartkowiak et al. 2017; Birmili et al. 2006; Majid 2011; Neal et al. 2005; Pett-Ridge 2009; Zhang 2004). The enrichment of P in stable inorganic forms (residual P) may reflect the P contained in construction materials such as asphalt, wood and cement from buildings and pavements (Ahmed and Ishiga 2006; Amato et al. 2009; Metson et al. 2012). Even more relevant for the urban soils of this study, which were visibly free from technogenic materials, is a probably higher contribution of stable primary minerals and rock fragments. Phosphorus in these geogenic materials was determined by pressurized acid digestion (total P and residual P calculated from that) but not by 1-h shaking with HCl (fifth step of the sequential extraction procedure). Harrell and Wang (2006) termed the residual fraction as “most chemically stable inorganic and organic P forms”.

The river soils from both sites upstream and downstream of the city were especially enriched in labile P (14.9 and 57.4 mg kg⁻¹ NaHCO₃-P, respectively), with clear difference between sites (Fig. 2a). Increased labile P can result from

the higher moisture of these soils in the otherwise semiarid landscape; soil moisture significantly affects P availability (DeLonge et al. 2013). This does not explain the difference between the upstream and downstream sites, but additional translocation of P from terrestrial soils into surface waters and adjacent river soils must be considered. The river banks upstream, with 0.6 g kg^{-1} total P, possibly received input from rural soils, while the even higher total P downstream (river banks downstream 0.8 g kg^{-1} total P) pointed to additional input from urban activities; this matches with the above-stated high risk of labile P losses from urban soils. In general, it is confirmed that arable, and even more so urban, land use contributes to P in surface waters and the respective soils (Smil 2000; Vidmar et al. 2016; Yong and Chen 2002). For example, a similar accumulation of P in downstream versus upstream soils was found in the watershed of the greater London Authority Area (Meng et al. 2017). Zhang et al. (2018) even concluded that upstream areas act as P sources, while downstream areas are sinks of P inputs. Nonetheless, the input of urban wastewater is clearly the primary source of P enrichment in downstream soils, as was shown for example for the Al-Khair River in Baghdad (Al-Ghazali and Khorshed 1988).

Calcareous arable soils are often characterized by very low contents of easily available P species due to the formation of secondary Ca-phosphates from fertilizer P (For et al. 1993; Naidu and Rengasamy 1993; Shen et al. 2019). This was confirmed in this study based on the much higher CB-P contents in arable compared to all other soils, indicating labile pedogenic Ca-phosphates (Harrell and Wang 2006). Furthermore, depletion of the labile fraction by plant uptake and withdrawal by harvest (Bittman et al. 2017; Leinweber et al. 1999), as well as loss of available P via leaching as a result of long-term artificial irrigation (Harun et al. 2013), may explain the lower easily or plant available P ($\text{NaHCO}_3\text{-P}$) in the arable versus urban soils. The influence of arable land use was also reflected by the significantly lower IC contents and an increase in Fe-associated P species and fractions in arable compared to urban soils, as determined by P XANES analysis and chemical fractionation, respectively. Application of acidic mineral fertilizer and decomposition of organic fertilizer substrates likely contributed to the shift from Ca-phosphates to Fe-phosphates in arable soils. Furthermore, intensified losses of carbonates and continuous inputs of dissolved Mn(II) and Fe(II) with irrigation water that subsequently oxidize and precipitate in terrestrial soils are typical features of long-term irrigation (Aziz and Smith 1992; Cornell and Schwertmann 2003). As a consequence and consistently confirmed by P fractionation and P XANES analysis, arable land use resulted in increased proportions of Fe-associated P (CBD-P) and decreased proportions of Ca-associated P, whereas urbanization increased proportions of Ca-associated P (Tables 1, 5).

Conclusions

Different land use does not necessarily alter total P. Hence, the total P content of soil as a sole parameter is unable to reveal the impact of urbanization on P status and speciation in calcareous soils. In this study, this is demonstrated based on rural and urban soils from the region of Sulaimani city. Methodologically, the combination of sequential P fractionation and P K-edge XANES spectroscopy is suitable to identify land use effects on the P distribution among P species and fractions of different P solubility and availability. A pattern of P species with prevalent Ca-phosphates is a typical feature of calcareous soils in semiarid regions. This pattern is clearly affected by human impacts such as arable and especially urban land use.

It is postulated that significantly higher contents of labile and easily available P as well as stable inorganic (residual) P represent a characteristic, uniform pattern of P fractions in urban soils. Correlation analysis of P data and general soil properties such as the content of organic matter and pedogenic oxides is even better suited to elucidate changes in P distribution. The fact that in this study almost no significant correlations were found for urban soils (in contrast to rural soils) reveals that the P distribution among fractions in urban soils is disrupted from natural pedogenetic processes. The impact of urban soil use on P forms is a long-term process; in the rather young Sulaimani city it was not strong enough to result in differences between different urban areas. It is concluded that, due to the altered soil properties and P speciation, urban soils can contribute to P contamination of other environmental compartments. In agreement with the substantial enrichment in labile P and P in solution in urban soils, river soils from downstream sites had especially high contents of labile P fractions.

Organic P species are apparently of subordinate relevance in calcareous, high-pH soils. Note, however, that the extraction scheme used here was not explicitly designed to determine organic P. This calls for further research on organic P species in urban versus rural soils.

Acknowledgements We thank H.K. Kamal, K.Z. Al-Janabi and M. Qadir, University of Sulaimani, for valuable support in soil sampling and soil identification. O. Baeza Urrea, A. Marx, M. Ortner, and P. Ziegler, University of Trier, kindly contributed to the XRD analyses and other analytical work. The P K-edge XANES research described in this paper was performed at the Canadian Light Source (CLS), which is supported by the Canadian Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research. We are indebted to all the colleagues at CLS for enabling the XANES research by J. Kruse and to P. Leinweber, University of Rostock, for supportive advice. 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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