



# Exploiting biogeochemical and spectroscopic techniques to assess the geochemical distribution and release dynamics of chromium and lead in a contaminated floodplain soil



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## HIGHLIGHTS

- New combination of biogeochemical and spectroscopic techniques.
- SEM–EDX images demonstrate concomitant occurrence of Pb, Mn, Fe, and Al.
- Coexistence of Cr and Fe was detected.
- Aromatic carbon identified by <sup>13</sup>C NMR spectroscopy dominated in this floodplain soil.
- Release of Cr, Pb, Fe, and Mn increased under acidic oxic conditions.

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## ABSTRACT

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) combined with a seven steps sequential extraction technique were used to assess the geochemical distribution of chromium (Cr) and lead (Pb) in a contaminated floodplain soil. Total contents of Cr and Pb were 490.3 and 402.1 mg kg<sup>-1</sup>, respectively. The residual fraction was 59.5 and 56.3% of total Cr and Pb. The crystalline iron (Fe) oxide was the dominant non-residual fraction of Cr (35.9% of total Cr). Considerable amounts of Pb were found in the organic fraction (35.4%). Using <sup>13</sup>C nuclear magnetic resonance spectroscopy, the soil organic matter was identified as 48.9% aromatic carbon, which indicated that a certain portion of Pb and Cr might be associated with aromatic compounds. The SEM–EDX images demonstrate a concomitant occurrence of Pb, manganese (Mn), Fe, and aluminum (Al) as well as a coexistence of Cr and Fe.

The release dynamics of dissolved Cr and Pb as affected by redox potential (E<sub>H</sub>), pH, Fe, Mn, dissolved organic carbon, and sulfate was quantified using an automated biogeochemical microcosm apparatus. Soil pH decreased under oxic conditions. The release of Cr, Pb, Fe, and Mn increased under acidic oxic (pH = 3.7, E<sub>H</sub> = 521 mV) conditions due to the associated decrease of pH (7.1–3.7). The mobilization of Cr and Pb was affected by the Fe and Mn. In conclusion, our multi-technique approach identified the geochemical distribution of Cr and Pb and verified major factors that explain mobilization of Cr and Pb in floodplain soils.

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## 1. Introduction

Soils in floodplain ecosystems are frequently polluted by

potentially toxic metals (PTMs) (Rinklebe et al., 2007; Schulz-Zunkel et al., 2015; Shaheen et al., 2014a,b). Elevated levels of PTMs, including chromium (Cr) and lead (Pb) in acidic soils may increase the solubility, phytoavailability, and leaching of these metals resulting in an adverse impact on the agricultural environment (Du Laing et al., 2009; Frohne et al., 2015; Ok et al., 2011; Overesch et al., 2007; Rinklebe et al., 2016a; Shaheen and

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Rinklebe, 2015a,b). Pollution by Cr and Pb is a global environmental concern and a significant issue for environmental protection because Cr and Pb are toxic and potentially mobile (Rinklebe and Shaheen, 2014; Shaheen and Rinklebe, 2014).

Total content of PTMs has been used to assess the risk of soil pollution by comparing it with background or guideline values of PTMs, and creating a pollution index such as the enrichment factor, geo-accumulation index, contamination factor and complex quality index (Rinklebe and Shaheen, 2014). However, it is insufficient to use the total content of PTMs in soil for an environmental risk assessment because the mobility of PTMs depends on their binding forms (Pueyo et al., 2008; Rinklebe and Shaheen, 2014). Therefore, determining the geochemical fractions of PTMs is appropriate to assess their potential mobility and pollution status in soils and it is therefore a key issue in many environmental studies (Rinklebe and Shaheen, 2014; Shaheen et al., 2015a; Zimmer et al., 2011). Chemical extraction procedures have been extensively employed to determine elemental distribution among the geochemical fractions in contaminated soils (Pueyo et al., 2008; Shaheen and Rinklebe, 2014). However, the precision of these techniques is limited, since re-adsorption and redistribution of the target element can occur during the extraction procedures; and thus, the concentration of the target element can be over or under estimated (Khaokaew et al., 2011; Ostergren et al., 1999). Therefore, to assess the mobilization and toxicity of PTMs in soil, their compartmentalization in the soil and their association with soil components that can potentially change their chemical properties has to be determined (Khaokaew et al., 2011; Landrot et al., 2012). Spectro-microscopic techniques are being increasingly used in different research areas to study the distribution of elements in diverse matrices (Ahmad et al., 2014a,b; Hashimoto and Yamaguchi, 2013; Khaokaew et al., 2011, 2012; Landrot et al., 2012).

The distribution of PTMs including Cr and Pb between the liquid and solid phase of floodplain soils and their release dynamics is mainly affected by soil properties and by changes of redox potential ( $E_H$ ), soil pH, and metal carriers such as iron (Fe), manganese (Mn), dissolved organic carbon (DOC), and sulfate ( $SO_4^{2-}$ ) (Rinklebe et al., 2016a,b; Rupp et al., 2010; Schulz-Zunkel et al., 2015; Shaheen et al., 2013; Shaheen et al., 2014a, 2016,b,c). A proper understanding of the geochemistry of Cr and Pb in floodplain soils is limited particularly under dynamic reducing-oxidizing conditions. Moreover, the association of Cr and Pb with different soil components such as soil organic matter (SOM), pedogenic Fe, Mn, and Al oxides in floodplain soils using a scanning electron microscope (SEM) coupled with energy dispersive X-ray analysis (EDX) is not well studied up to date. However, it is essential to understand the geochemical behavior of Cr and Pb in floodplain soils for a better prediction of their mobilization, hazard and eco-toxicity. Additionally, detailed knowledge about the distribution of Cr and Pb among the geochemical fractions and their release dynamics in floodplain soils is required to understand their general mobilization processes and enable a more accurate prediction of Cr and Pb release into surface-, ground-, and river waters in response to changing redox conditions. Therefore, the overall objective of the study is to assess both, the geochemical distribution and the release dynamics of Cr and Pb in a contaminated floodplain soil using a combination of geochemical and spectroscopic techniques. The specific objectives are 1) to determine the geochemical fractions of Cr and Pb in a contaminated floodplain soil using a seven steps sequential extraction technique, 2) to determine the distribution of Cr and Pb and other elements using the SEM–EDX technique, and 3) to quantify the impact of  $E_H$ , pH, Fe, Mn, DOC, and  $SO_4^{2-}$  on the release dynamics of dissolved Cr and Pb.

## 2. Materials and methods

### 2.1. Collection and characterization of the soil

Soil sampling was carried out at the floodplain at the lower course of the Wupper River, close to the confluence into the Rhine River, Germany (E 2570359, N 5661521; 51°4′0.48″N, 6°4′0.48″E). The long term annual precipitation is approximately 774 mm and the long term annual air temperature is 10.8 °C (DWD, 2009). The site is used as grassland and periodically flooded by the Wupper River, usually in spring time. More details about the study site are available in Frohne et al. (2011, 2014); Rinklebe and Shaheen (2015); Shaheen et al. (2015b). The sample was collected from a soil profile at 24–46 cm depth since this horizon reveals the highest contamination with PTMs. About 400 kg soil was collected from an area of 4 m<sup>2</sup>. The sampling was performed in eight replicates of about 50 kg which were pooled to one composite sample. Soil material was carefully homogenized, air-dried and crushed handily. All results presented here have been carrying out on exactly the same soil sample. Soil properties were determined according to standard methods (Blume et al., 2011). The mineralogical composition of the sample was characterized by X-ray diffractometry with a Bruker AXS 500. We used Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at 40 kV and 40 mA with step-scanning from 3 to 69 °2 $\theta$  at a step size of 0.05 °2 $\theta$  and a counting time of 1.5 s per step. Chemical characteristics of the sample's SOM were analyzed by solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy with a DSX 200 spectrometer (Bruker, Ettlingen, Germany). We applied the cross-polarisation magic angle spinning technique with a <sup>13</sup>C-resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz. A ramped <sup>1</sup>H-pulse starting at 100% and decreasing to 50% of the initial power was used during a contact time of 1 ms to circumvent spin modulation during the Hartmann-Hahn contact. The pulse delay was 1 s, 177189 spectra were accumulated, and we applied a line broadening between 0 and 50 Hz. The <sup>13</sup>C chemical shifts were calibrated relative to tetramethylsilane (0 ppm). We determined relative contributions of the various functional groups by integrating the signal intensity in the respective chemical shift regions according to Knicker and Lüdemann (1995): carbonyl (aldehyde and ketone) and carboxyl/amide C (220–160 ppm), olefinic and aromatic C (160–110 ppm), O-/N-alkyl C (110–45 ppm) and alkyl C (45 to –10 ppm). When integrating these regions, we considered spinning side bands by adding their intensities to those of their parent signals.

### 2.2. Geochemical fractionation of Cr and Pb

The soil sample was sequentially extracted to determine seven geochemical fractions of Cr and Pb based on the work of Zeien and Brümmer (1989) and proposed by Rinklebe and Shaheen (2014) and Shaheen and Rinklebe (2014). Briefly, 2 g of air dried soil (<2 mm) and 50 ml extracting agent were shaken (overhead 20 rotations min<sup>-1</sup>) at 20 °C. The samples were centrifuged for 10 min at 3000 rpm and filtered (592, Schleicher and Schuell, Dassel, Germany). The extracting agents and common interpretation of fractions are as follows: F1: 1 M NH<sub>4</sub>NO<sub>3</sub> (soluble + exchangeable fraction), F2: 1 M NH<sub>4</sub>-acetate (easily-mobilized fraction), F3: 0.1 M [NH<sub>3</sub> (OH)]Cl + 1 M NH<sub>4</sub>-acetate (bound to Mn (hydr-)oxides), F4: 0.025 M NH<sub>4</sub>-EDTA (bound to soil organic matter (SOM)), F5: 0.2 M NH<sub>4</sub>-oxalate buffer (bound by low crystalline Fe (hydr)oxides), F6: 0.2 M NH<sub>4</sub>-oxalate buffer + ascorbic acid (bound by crystalline Fe (hydr)oxides), F7: Aqua Regia (residual fraction). Separate subsamples were digested in a microwave system (Milestone MLS 1200 Mega, Germany) for total concentrations of Cr and Pb (US EPA 3051a, 2007).

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