



# Geochemical fractions of chromium, copper, and zinc and their vertical distribution in floodplain soil profiles along the Central Elbe River, Germany



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## ABSTRACT

The determination of geochemical fractions of heavy metals (HM) in soils is a key issue when studying their mobility. Therefore, we have determined the geochemical fractions and the vertical distribution of chromium (Cr), copper (Cu), and zinc (Zn) in seven floodplain soil profiles in relation to flooding conditions and relevant soil properties. These soil profiles represent two different soil groups (Mollic Fluvisols and Eutric Gleysols) which differ significantly in flooding duration and soil properties. The metals were fractionated sequentially to seven fractions as follows: F1: soluble + exchangeable, F2: easily mobilizable, F3: bound to Mn oxides, F4: bound to soil organic matter (SOM) (might include sulphides), F5: bound to low crystalline (amorphous) Fe oxides, F6: bound by crystalline Fe oxides, and F7: residual fraction.

The total Cr, Cu, and Zn concentrations ranged from 54.4 to 134.1, 165.2 to 215.7, and 128.5 to 1097.8 mg kg<sup>-1</sup>, respectively, and exceeded the precautionary values of the BBodSchV (1999). Total metal concentrations correlated significantly to soil organic carbon (SOC), total sulphur (S<sub>t</sub>), and cation exchange capacity (CEC), as well as crystalline and amorphous Fe- and Mn-oxides. The residual fraction was dominant for Cr, the organic bound for Cu, and crystalline Fe oxides for Zn. The potential mobile fraction (PMF = ∑ F1–F6) ranged from 38.4 to 71.4, 63.9 to 85.1, and 51.5 to 83.3% of the total Cr, Cu, and Zn, respectively. However, the mobile fraction (MF = ∑ F1–F2) ranged from 0.96 to 1.84, 2.1 to 4.1, and 9.1 to 28.7% of the total concentrations of Cr, Cu, and Zn, respectively. The order of the PMF in the studied soil profiles was Cu > Zn > Cr, while the order of the MF was Zn > Cu > Cr. The PMF of the three metals was positively correlated with SOC and Mn oxides. The PMF was positively correlated with CEC (Cr, Zn), S<sub>t</sub> (Cr), and Fe oxides (Zn). The PMF of Cu and Zn correlated negatively with clay. The MF of the three metals was correlated negatively with soil pH. The MF of Zn was correlated positively with clay, SOC, and S<sub>t</sub>. The MF of Cr was correlated positively with clay, while it correlated negatively with SOC, S<sub>t</sub>, CEC, and Fe–Mn oxides. The Fluvisols revealed higher total concentrations and potential mobilities of Cr, Cu, and Zn compared to the Gleysols. However, the Gleysols had a higher metal mobility compared to Fluvisols due to their longer flooding duration. The solubility of Cr below the average water level in the studied profiles was higher than above the water level, while the solubility of Cu and Zn above the water level was higher than below the water level in both soil groups. The potential mobility of the studied metals (especially of Cu followed by Zn), and thus the transfer of these metals into the grassland and food chain, should be high, which might be harmful to the floodplain ecosystem.

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## 1. Introduction

Heavy metals (HM) in soils are toxic to plants, animals, and humans due to their possible transport into the food chain. Total concentrations of HM might serve as useful indicators for an appropriate assessment of the contamination status of soils. However, they are not able to provide sufficient information about the bioavailability, mobility, and toxicity of

HM (Zhong et al., 2011). The mobility and release of HM in soils depends on their total concentration, specific chemical form, binding state, the metal properties, environmental factors, and soil properties. Therefore, determination of the binding forms of HM into different geochemical fractions is needed to evaluate their mobility and pollution status in soils (Hooda, 2010). Heavy metals exist in various fractions such as soluble + exchangeable, carbonate-associated, Fe–Mn oxides associated, OM associated, and residual fractions. Among these fractions, soluble + exchangeable and the easily mobilizable fraction are considered to be bioavailable and mobile fractions (MF). The potential mobile fractions (PMF) of HM, including the non-residual fractions (i.e., carbonate-, Fe–Mn oxides-associated, and OM-bound

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fractions), can also be bioavailable if the pH and redox potential of the soil change (Ma and Rao, 1997).

Sequential extraction procedures are widely applied for assessing HM fractionation and bioavailability in soils (Doelsch et al., 2008). Numerous fractionation techniques have been used for the sequential extraction of HM in soils (Rauret et al., 1999; Sposito et al., 1982; Tessier et al., 1979). These techniques vary in the number of fractions extracted as well as in the order and kind of reagents used. However, most of these techniques deal with the Fe/Mn oxide fraction as one fraction. One advantage of our technique (Zeien and Brümmer, 1989) is that we were able to fractionate this fraction into three different fractions i.e., manganese oxide fraction (bound to Mn(hydr)oxides), amorphous iron oxide fraction (bound by low crystalline Fe (hydr)oxides), and crystalline iron oxide fraction (bound by crystalline Fe (hydr)oxides).

Past research has paid relatively little attention to wetland soils, especially floodplain soils, which have been less studied compared with terrestrial soils although they frequently reveal high levels of pollutants (Rinklebe et al., 2007). Floodplain soils are formed by the periodical deposition of suspended sediments from river water during flood events. Because of their generally high fertility, some floodplain soils have also been intensively used for agriculture for a long time. Today, additional considerable risk is associated with the often very high levels of metals in floodplain soils (Overesch et al., 2007). Over decades the River Elbe, including its tributaries, has become one of the worst polluted major rivers of Europe, carrying high concentrations of HM (e.g., Du Laing et al., 2009; Zimmer et al., 2011). Previous studies have detected Mollic Fluvisols and Eutric Gleysols as the most contaminated soil types in floodplains (e.g., Rinklebe, 2004; Rinklebe et al., 2007). However, considerable knowledge gaps exist regarding the fractionation and depth distribution of HM in these soil groups. A few studies about the fractionation of HM have been conducted in floodplain soils at the Elbe River (Rennert et al. 2010; Zimmer et al., 2011). However, these were conducted in top soils only, not in complete soil profiles. In addition, the relationships between soil properties and the vertical distribution of different metal fractions in various floodplain soil types have not been studied to our knowledge to date. Therefore, our objectives were 1) to fractionate and compare the binding forms of Cr, Cu, and Zn, 2) to assess the vertical profile distribution and mobility of Cr, Cu, and Zn, as affected by relevant soil properties, and 3) to define the impact of flooding duration and contamination levels on metal fractionation in the soil profiles of three Mollic Fluvisols and four Eutric Gleysols along the Central Elbe River, Germany.

## 2. Material and methods

### 2.1. Study areas and study sites

The Elbe River is 1162 km long and has a catchment area of 148,268 km<sup>2</sup> (Vogt et al., 2007). It is the third largest river of Central Europe in terms of its length and the size of its catchment area. The three study areas are located in floodplains of the Central Elbe River in Germany. The Wörlitz site is situated on stream kilometer 242 (51°51'27"N, 12°23'06"E), the Steckby site on stream kilometer 284 (51°54'51"N, 11°58'33"E), and the Sandau site on stream kilometer 417 (52°48'00"N, 12°02'15"E) (Fig. 1).

The long-term annual precipitation ranges from 470 to 570 mm and the mean annual air temperature is approximately 8.0 °C (Rinklebe, 2004). Seven study sites were selected within these three study areas after large-scale conventional soil mapping and several years of comprehensive field pedological research in the floodplains of the Elbe River (e.g. Rinklebe and Langer, 2006; Rinklebe et al., 2005). The specific study sites represent common and frequently polluted soil units at the Elbe River. The former studies have shown high metal contaminations of soils at these sites (Overesch et al., 2007; Rinklebe et al., 2007). The sites are used as extensive grassland, pasture or fallow. All study sites

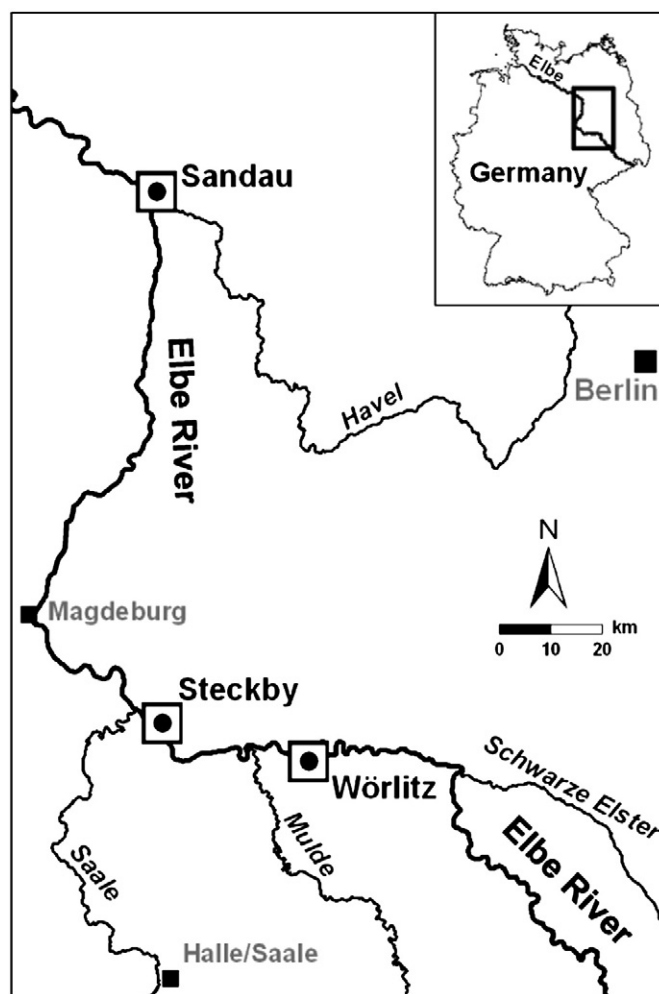


Fig. 1. Location of the study areas at the Elbe River in Germany.

are periodically flooded, mainly depending on snow melt (winter and spring) and heavy rainfalls (spring and summer).

Water level (WL) characteristics during 26 months and the altitude of the studied floodplain soil profiles were measured in previous studies (Rinklebe, 2004). At the respective sites a soil-hydrological monitoring station was set up to determine soil redox potential ( $E_H$ ) in different depths. Five replications at each depth were carried out to cover soil heterogeneity. Redox potential ( $E_H$ ) was measured using a platinum (Pt) electrode against a silver–silver chloride (Ag/AgCl) reference electrode; each was placed in the middle of the respective soil horizon. Data were stored every two hours using data loggers. These original data were aggregated to mean daily values which were used for the given descriptive statistics.

### 2.2. Sampling, pre-treatment, and analysis of soil

At each study site, soil samples were collected in soil profiles to a depth of more than 1 m or until humus- and clay-poor sand was reached. Sampling was performed in four replicates of about 1 kg, which were pooled to one sample per horizon (Rinklebe, 2004). Soil material was air dried and sieved to <2 mm. Subsamples were ground in an agate disc mill. Briefly, the soil properties were determined according to standard methods (Blume et al., 2011) as follows: total C ( $C_t$ ) and total N ( $N_t$ ) were measured with dry combustion and thermal conductivity detection using a C/N/S-Analyser (Vario EL Heraeus, Fa. Analytik Jena). The concentrations of inorganic C ( $C_{inorg}$ ) were determined by the Scheibler-method (Blume et al., 2011). Soil organic carbon (SOC) was calculated as the difference between  $C_t$  and  $C_{inorg}$ .

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