Chromium Release from a COPR-Contaminated Soil at Varying Water Content and Redox Conditions

Katrin Matern and Tim Mansfeldt*

Abstract

Many soils in the region of Kanpur, North India, are heavily affected by the leather industry and its upstream supplier sector, as indicated by elevated chromium (Cr) contents. Under reducing conditions—for instance, at water saturation after monsoon rain or flood irrigation—the dynamic and species distribution of Cr may be affected due to changes in redox potential (E°). In this study, the influence of E° on the speciation and release of Cr from a contaminated agricultural soil was investigated. A soil sample that was affected by hyperalkaline leachate from chromite ore processing residue, was taken and packed in soil columns, and subjected to a saturation–drainage–saturation cycle. After initial water saturation, the E° dropped slowly to minimum values of around −100 mV (calculated to pH 7), while E° was controlled by CrO_4^{2−}/Cr_2O_7^{2−}, or CrO_4^{2−}/(Fe,Cr)OOH redox couples. Soil drainage resulted in a quick return to oxidizing conditions; i.e., E° > 300 mV. The Cr species distribution and release showed a clear trend with E°. At the beginning of the experiment, under oxidizing and weakly reducing conditions (E° range from >100 to 300 mV), Cr(VI) was released in particular. However, under moderately reducing conditions (E° range from 100 to −100 mV), Cr was gradually immobilized and irreversible sequestered via reductive precipitation. The results presented in this study provide an improved understanding of the mobility of Cr(VI) in contaminated soils at varying water contents, which is essential for the evaluation of environmental risks in this region.

Core Ideas

- Cr(VI) was highly mobile in the investigated soil.
- High Cr(VI) concentration prevented the reduction of Mn and Fe.
- Cr(VI) was mobilized under oxidizing soil conditions.
- Cr was immobilized under moderately reducing soil conditions.

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*Corresponding author (tim.mansfeldt@uni-koeln.de).

CHROMIUM (Cr) is introduced into the environment from industrial activities, including mining of chromite, metallurgical, electroplating, production of paints and pigments, and leather tanning (Kimbrough et al., 1999). Extensive Cr contamination occurs in the area of Kanpur, in the State of Uttar Pradesh, North India, which is a prominent center for leather-processing clusters of tannery industries. Waste from these tanneries and related industries has polluted plants, soils, sediments, rivers, and ground waters of the surrounding Ganga Plain (Anvari et al., 1999; Sinha et al., 2006; Srivinasa Gowd et al., 2007; Singh et al., 2009; Srivinasa Gowd et al., 2010). Basic Cr(III) sulfate (BCS) plays a central role in the tanning of leather, and is produced by the chromate (CrO_4^{2−}) extraction roasting process in the industrial suburbs of Kanpur. Therefore, a high-time processing technique is used to oxidize the Cr in the ore from insoluble Cr(III) to soluble Cr(VI), followed by aqueous leaching ( Antony et al., 2001; Darrie, 2001; Tathavadkar et al., 2001). This technique produces so-called chromium ore processing residue (COPR), which is landfilled in large amounts. The water emerging from these COPR landfills contaminates surrounding soils and groundwater.

The mobility, bioavailability, and toxicity of Cr in the environment depend on its oxidation state (Avudainayagam et al., 2003; Agnieszka and Barbara, 2012). In the environment, Cr can be present as Cr(III) or Cr(VI). While Cr(III) is relatively immobile in soil, and according to today’s knowledge, is essential for plants, animals, and humans, Cr(VI) is highly mobile and results in significant human health and ecological risks (Rifkin et al., 2004; Johnson et al., 2006; Dhal et al., 2013). Aqueous concentrations of Cr are mainly controlled by adsorption, mineral dissolution, and precipitation. Chromium(VI) is adsorbed by various mechanisms onto aluminum and iron oxides, especially at low pH values (Mesuere and Fish, 1992; Hsia et al., 1993; Abdel-Samad and Watson, 1997; Fendorf et al., 1997). Chromium(III) is also strongly retained by minerals, whereby Cr(III) is predominantly adsorbed at higher pH values. Additionally, at pH >5.5, Cr(III) precipitates as a sparingly soluble amorphous Cr(III)-hydroxide. Only if complexed with organic acids, such as citric acid, can Cr(III) remain soluble at pH ≥6.7 depending on pK, and concentrations of complexing ligands (James and Bartlett, 1983).

Abbreviations: E°, redox potential; COPR, chromite ore processing residue; BSC, basic chromium sulfate; Fe_2, oxalate-extractable (short-range-ordered); Fe_3, dithionite-citrate extractable (pedogenic) Fe; SOM, soil organic matter.
When soils are inundated, for instance, during water saturation after monsoon rain or flood irrigation, the change in the water table may result in frequent oscillations in redox potential ($E_{H^+}$). Upon water saturation, the redox status can change from oxidizing ($E_{H^+} > 300$ mV at pH 7) to strongly reducing ($E_{H^+} < -100$ mV at pH 7) soil conditions (Reddy and DeLaune, 2008). Resulting redox-sensitive processes affect the dynamics of Cr in soils (Hindersmann and Mansfeldt, 2014; Couture et al., 2015; Frohne et al., 2015), either directly by changes in its speciation, or indirectly, via changes in pH, concentration of dissolved organic carbon, or the redox chemistry of Fe, Mn, and S compounds (Du Laing et al., 2007, 2009). Couture et al. (2015) investigated the mobilization of contaminants in soils during redox oscillations, and pointed out that Cr was present under oxidizing conditions, and irreversibly sequestered via reductive precipitation under low $E_{H^+}$. In contrast, Frohne et al. (2015) and Hindersmann and Mansfeldt (2014) figured out that Cr was significantly and negatively correlated with $E_{H^+}$, due to the possible co-precipitation of Cr with Fe (hydr)oxides at high $E_{H^+}$ and reductive dissolution of Fe (hydr)oxides and the related mobilization of Cr under low $E_{H^+}$.

The aim of the study was to investigate the influence of reducing conditions on the release of Cr from a soil, which was affected by hyperalkaline leachates from COPR. Therefore, a soil sample from an agriculture field close to a COPR dumping site was taken. Redox conditions were assessed by measuring the $E_{H^+}$ during a saturation–drainage–saturation cycle. These conditions occur naturally during monsoon or flooding events in the context of farming (e.g., rice cultivation). We expect that changes in $E_{H^+}$ significantly affect the speciation and leaching of Cr. The redox-related changes in speciation, as well as the influence of other controlling factors, such as pH and pedogenic (hydr)oxides, might be important factors. Indeed, Cr mobilization from contaminated soils has been investigated before (Hindersmann and Mansfeldt, 2014; Shaheen et al., 2014; Couture et al., 2015; Frohne et al., 2015). However, the studies thus far focused on floodplain soils, with sources of contamination that differ from our investigated soil. We expect that COPR leachates due to their specific chemical composition significantly influence the redox behavior and thus the mobility and transport of Cr(VI) in soils. Furthermore, the experimental setup was different, since the previous studies used microcosm systems with soil slurry instead of soil columns. Soil columns enable a more realistic spatial distribution of the soil, whereas microcosm systems lead to higher reactive surface that may result in enhanced kinetic rates. The combined detailed investigation of Cr distribution and speciation in polluted agriculture soils can reveal prevalent Cr reduction and transport pathways. This knowledge is required for proposing adequate measures to counteract negative effects of Cr(VI) pollution, especially in COPR polluted areas.

**Materials and Methods**

**Study Site, Sampling, and Sample Preparation**

The soil sample was taken from an agriculture field in Godhrauli, Uttar Pradesh, North India. This sampling location was close to a COPR dumping site (Supplemental Fig. S1). The waste was obtained from a BCS manufacturing unit, located 7 km away in Chhewali, and was deposited illegally over the past few years. During the monsoon, Cr is leached out from the COPR waste and flushed over the field. Before sampling, the first 5 cm of the soil surface was removed to avoid impurities from COPR material. The sample was manually homogenized, air-dried, and sieved to <2 mm. For C and N, and aqua regia analysis, subsamples of the fraction <2 mm were ground in an agate ball mill (PM 400, Retsch, Haan, Germany).

**Characterization of the Soil Samples**

Particle size distribution was analyzed by wet sieving and sedimentation, using the pipette sampling technique. Before the analyses, soil organic matter (SOM) was destroyed with H$_2$O$_2$, and carbonates were destroyed with HCl. Soil pH was measured potentiometrically, using a glass electrode (Unitrode, Metrohm, Filderstadt, Germany) in both 0.01 M CaCl$_2$ solution and deionized water, with a solid/solution ratio of 1:5. Total C and N were quantified with a CNS analyzer (Vario EL, Elementar, Hanau, Germany). Organic C was determined with the same equipment by adding 10% HCl to the weighed samples. Inorganic C was calculated as the difference between total and organic C. Contents of oxalate-extractable Fe (Fe$_{ox}$) were determined according to Schwertmann (1964), and dithionite-citrate extractable Fe (Fe$_{d}$) according to Mehra and Jackson (1960). The concentrations of Mn and Fe were measured by flame atomic absorption spectrometry (iCE 3500, Thermo Scientific, Dreieich, Germany), with an air-acetylene flame. Contents of Mn, Fe, and Cr were also determined with a pseudo-total microwave-induced (Ethos, MLS, Leutkirch im Allgäu, Germany) aqua regia digestion. Therefore 0.2 g of ground sample was weighed into a PTFE liner. Then 2 mL of concentrated HNO$_3$, and 6 mL of concentrated HCl (Suprapur, Merck, Darmstadt, Germany) were added. After microwave digestion, the samples were filtered through a quantitative filter (5–10 µm, VWR, Darmstadt, Germany), and made up to a final volume of 50 mL with deionized water. Iron and Mn were measured as described before, and Cr (>1 mg L$^{-1}$) was determined by atomic absorption spectrometry with a nitrous oxide-acetylene flame. Chromium(VI) in the soil was extracted with a carbonate-hydroxide solution (0.28 M Na$_2$CO$_3$ in 0.5 M NaOH, pH 11.8–12.3), according to James et al. (1995), and analyzed spectrophotometrically at 550 nm (Lambda 25 UV/Vis Spectrometer, Perkin-Elmer, Rodgau, Germany) with diphenylcarbazide, according to the US EPA (1992). Binding forms of Cr were analyzed in triplicate, following the sequential extraction scheme of Zeien and Brümmer (1989). The method provides seven fractions, operationally defined as: the mobile fraction (F1), exchangeable fraction (F2), bound to Mn oxide (F3), organic bound fraction (F4), bound to short-range-ordered Fe (hydr)oxide (F5), bound to crystalline Fe (hydr)oxide (F6), and residual pools (F7). If the Cr concentration was <1 mg L$^{-1}$, it was analyzed by inductive coupled plasma mass spectrometry (ICP–MS, X-Series II, Thermo Scientific, Dreieich, Germany). Otherwise it was measured as described before.

**Soil Column Experiment**

The column experiment was performed in duplicate with the homogenized soil fraction <2 mm. Aliquots for the column experiment were obtained by coning and quartering (Crosby and Patel, 1995). Supplemental Fig. S2 shows the design of the experimental setup. The soil material was poured into cylindrical polyethylene tubes (11 cm i.d., 25 cm length, 23 cm packed length) and compacted in layers with a plunger to achieve a bulk density...
of 1.3 g cm$^{-3}$. A porous plate with a polyamide membrane (porosity 80% v/v, ecotech, Bonn, Germany) was used as a base for the packed columns. The columns were equipped with polyether-sulfone suction cups with a pore diameter of 0.45 μm (custom design, Deltares, Utrecht, Netherlands). To determine the $E_{h}$, an Ag/AgCl electrode, filled with 3 M KCl (SE 23, Sensortechnik Meinsberg, Meinsberg, Germany) and platinum electrodes, according to Mansfeld (2003), were installed. The electrodes were connected to a data logger (LogTrans 16 GPRS, UIT, Dresden, Germany). The redox potential was recorded every 5 min and related to the standard hydrogen electrode by adding 207 mV to the measured value, hereafter referred to as the reference electrode. Additionally, $E_{h}$ (in units of mV) was converted to $E_{h}$ values at pH 7, that is $E_{h}$ (pH 7), from the measured pH of the soil solutions by

$$E_{h}(\text{pH 7}) = E_{h} + (\text{pH 7} - 7) \times 59$$  \[1\]

The assumption that there will be a shift of 59 mV for each increase of one pH unit should be considered with caution (Reddy and DeLaune, 2008), since this relationship is only valid for the oxidation–reduction reaction in which

$$mH^+ = ne^-, \text{ or } m/n = 1$$  \[2\]

However, the value of 59 mV per pH unit is probably as good a conversion factor as any, and the adjustment makes comparisons between different media more convenient (Bohn, 1971).

All instruments were inserted horizontally at the following positions above the porous plate: the suction cups were placed at 6, 13, and 20 cm; the platinum electrodes were placed at 7, 14, and 21 cm; and the reference electrode was placed at 12 cm.

Table 1 shows the sequence of the experimental steps and the adjusted matrix potentials (hPa). For saturation, the columns were upstream-fed with a degassed solution until the water level was 1.5 cm above the soil surface. The solution had the composition of typical monsoon rainwater according to Berner and Berner (1996) with 0.47 mg L$^{-1}$ Na, 0.23 mg L$^{-1}$ K, 0.23 mg L$^{-1}$ Mg$^{2+}$, 1.4 mg L$^{-1}$ Ca$^{2+}$, 0.92 mg L$^{-1}$ Cl$^{-}$, and 0.63 mg L$^{-1}$ SO$_4^{2-}$. To prevent evaporation, the columns were covered with a polyethylene wrap, which was perforated to enable gas exchange with the atmosphere. After saturation, the water content was lowered by removing water from the columns with a membrane vacuum pump (model M2, Vaucbrand, Wertheim, Germany). According to the equation by van Genuchten (1980), we calculated the volumetric water content at −10, −40, −60, and −100 hPa matric potentials. We estimated Van Genuchten Parameters by using the software Rosetta Lite v.1.1 (Schaap et al., 2001) and implemented soil data of percentage particle size fraction and bulk density.

During water saturation, and each matrix potential step, 6 mL pore water from each suction cup was sampled periodically (every 2–7 d). This volume was required to analyze various parameters. In the saturation period, the sample volumes were replaced with a syringe to retain a constant water surface. In total, 30 samples from each suction cup were taken during the experiment. In the samples, the soil solution pH was measured potentiometrically using a glass electrode (Unistrole, Metrohm). The solution concentrations of total Cr, Cr(VI), Fe (>0.5 mg L$^{-1}$), and Mn (>0.2 mg L$^{-1}$) were analyzed as described before. If concentrations of Fe were <0.5 mg L$^{-1}$ and of Mn were <0.2 mg L$^{-1}$, samples were measured by inductively coupled plasma mass spectrometry. Furthermore, concentrations of NO$_3^-$ and SO$_4^{2-}$ were determined by ion chromatography (ICS-1000, Dionex, Idstein, Germany).

**Reaction Calculation**

The reduction of Cr(VI) was calculated for the first saturation cycle by a first-order rate expression with respect to the Cr(VI) concentrations. A second-order rate expression with respect to the reduction of Cr by organic carbon was trialed but did not reproduce the measured data. Supplemental table S1 shows the redox half reactions and their theoretical equilibrium redox potential for dominant redox species.

**Results**

**Soil Properties**

Table 2 summarizes the main properties of the soil. The texture was dominated by silt with a texture of silty loam, according to FAO. Moreover, the soil was characterized by a pH of 8.4 (in CaCl$_2$). Furthermore, the soil had a relatively low organic C content of 4.87 g kg$^{-1}$. Besides, the soil sample contained

Table 1. Sequence of experimental steps and calculated pressure heats.

<table>
<thead>
<tr>
<th>Step</th>
<th>Adjusted matrix potential</th>
<th>Duration</th>
<th>Cumulative time</th>
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<td></td>
<td>hPa</td>
<td>d</td>
<td>d</td>
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<tr>
<td>Upstream infiltration</td>
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<td>0.25</td>
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<tr>
<td>Saturation</td>
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<td>62.17</td>
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<tr>
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<td>7.01</td>
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<tr>
<td>Saturation</td>
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<td>28.08</td>
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</table>

† According to FAO.
‡ Fe$_{d}$ oxalate-extractable Fe; Fe$_{d}$ dithionite-citrate extractable Fe.
3.36 g kg$^{-1}$ of total pedogenic Fe (Fe$_{tot}$), of which 1.06 g kg$^{-1}$ was short-range-ordered Fe (Fe$_{dr}$). Hence the Fe$_{dr}$/Fe$_{tot}$ ratio amounted to 0.32, indicating a larger proportion of crystallized Fe (hydr) oxides. Contents of Mn oxides were low, with 0.41 g kg$^{-1}$. Total Fe content was 25.0 g kg$^{-1}$, indicating that most of the Fe was residually bound. Sequential extraction revealed that Cr was associated predominantly with short-range-ordered (42.9% of total Cr) and crystallized Fe (hydr) oxides (27.1%), followed by the residual (18.7%) fraction (Supplemental Table S2). Chromium bound on Mn oxides, or on organic compounds, yielded only low amounts (together about 2.5%). Remarkable were the relatively high Cr concentrations in the mobile (4.54%) and exchangeable (4.20%) fraction that together amounted to 47.4 mg kg$^{-1}$. Considering that Cr(VI) contents amounted for 36.0 mg kg$^{-1}$, it can be assumed that most of the Cr(VI) is mobile in the investigated soil.

**Redox Potential and pH in Pore Water**

Figure 1a and b show the course of soil $E_{H}$ and pH in the pore water during the experiment. Changes in matrix potentials are indicated as vertical dashed lines. At the beginning of the experiment, the $E_{H}$ was between 400 and 500 mV in all sections of the column. After flooding of the soil, $E_{H}$ decreased slowly at first (100 mV in 20 d in the middle and 150 mV in 30 d in the lower
column section) and afterward rapidly to an $E_{H}$ of approximately −100 mV after 70 d, which corresponds to the beginning of strongly reducing conditions. Additionally, it should be noted that the lowest $E_{H}$ of the B column was around 50 mV higher than in the A column. Adjusting the matrix potential to −10 hPa did not have any effect on $E_{H}$. Only when the matrix potential was adjusted to −40 hPa (B column) and −60 hPa (A column), did the $E_{H}$ re-increase rapidly to oxidizing conditions (>300 mV). Re-saturation caused the $E_{H}$ to again decrease, but the decrease was distinctly more rapid than during the first period of saturation. Thus, the $E_{H}$ compiled with the values of the first saturation period in the middle and lower column sections. In the upper section of the column, the $E_{H}$ remained under oxidizing conditions throughout the experiment. Slight changes could be observed at the beginning of the experiment and during soil drainage.

As a general trend, the pH of the soil solution increased in all column sections during saturation and decreased after soil drainage. During the first period of saturation, the pH increased by 0.5 units, from 8.5 to around 9.0 in the upper section column, by 0.3 units from 8.6 to 8.9 in the middle column section, and by 0.7 (in A column) and 0.6 (in B column) units from 8.3 (in A) and 8.4 (in B) to 9.0 in the lower column section. After soil drainage, pH decreased by 0.2 units in the upper section and by 0.3 units in the middle and lower sections. In all column sections, the subsequent increase in pH upon the second period of saturation was not so high when compared to the first saturation period.

**Dynamics of Mn, Fe, NO$_3^-$, and SO$_4^{2-}$**

Higher Mn concentrations (>140 µg L$^{-1}$) in pore water were observed at low $E_{H}$ during saturation in the middle and lower sections of the column (Fig. 1c). In the upper section, a negligible increase in Mn concentrations up to 40 µg L$^{-1}$ could only be observed in the A column. Soil drainage led to a decrease of Mn concentrations up to 1 µg L$^{-1}$. After re-saturation, Mn concentrations again increased in the middle and lower sections, but not in the upper section. The course of Fe concentrations resembled those of Mn, but concentrations were in the mean distinctly lower (Fig. 1d). Furthermore, the course of Fe concentrations not only showed more fluctuations, but also higher differences between the two column parallels.

The course of NO$_3^-$ concentrations showed a similar trend as the E$_{H}$: high E$_{H}$ resulted in high NO$_3^-$ concentrations, and low E$_{H}$ resulted in low NO$_3^-$ concentration (Fig. 2a). Nitrate concentrations decreased rapidly during saturation, from >1000 mg L$^{-1}$ in the in the upper and lower column sections and >400 mg L$^{-1}$ in the middle column section to around 20 mg L$^{-1}$ within 34 d. At the end of the saturation period, only small NO$_3^-$ concentrations could be detected. During soil drainage, NO$_3^-$ concentrations increased in all sections up to >100 mg L$^{-1}$ (except in column A of the lower section, with 33 mg L$^{-1}$). In the second saturation period, NO$_3^-$ concentrations decreased again, but the values obtained before were not reproduced.

Sulfate concentrations also decreased distinctly during the first 40 d of the experiment, and subsequently reached a plateau in all column sections (Fig. 2b). No obvious trend could be observed for SO$_4^{2-}$ concentrations in response to the moisture regime, except for a distinct decrease after the second saturation period, following a plateau again. The decrease precedent was a slight increase in SO$_4^{2-}$ concentrations in the upper column section during soil drainage.

**Chromium Speciation and Mobilization**

Generally, Cr(VI) pore water concentrations decreased during saturation, and increased slightly after soil drainage in all column sections (Fig. 2c). Very high Cr(VI) concentrations (>100 mg L$^{-1}$ in the upper and lower sections, >50 mg L$^{-1}$ in the middle section) were present in the first samples, collected under saturation. These high Cr(VI) concentrations decreased up to <1 mg L$^{-1}$ in the upper section and to approximately 25 µg L$^{-1}$ in the middle and lower sections after 70 d. Chromium reduction was described well by the first order kinetic reaction with $R^2$ ranging from 0.95 to 0.99 (Supplemental Table S3). The lowest rate constants (3.9 and 5.4 s$^{-1}$) were found in the upper column section, which was caused by elevated $E_{H}$. Higher rate constants were found in the middle (12.6 and 17.4 s$^{-1}$) and lower (9.2 and 11.3 s$^{-1}$) column sections. Jamieson-Hanes et al. (2012) reported that Cr reduction follows a near zero-order rate expression at high concentrations and a first order rate expression when the concentration approached or was below the value of $K_{cr3}$. However, a linear Cr reduction could not be observed for our experiment, indicating that Cr reduction is dependent on Cr concentration. Soil drainage caused an increase in Cr(VI) concentrations up to 5 mg L$^{-1}$. In the second saturation period, Cr(VI) concentration again decreased up to 1 mg L$^{-1}$ in the upper section and to <20 µg L$^{-1}$ in the middle and lower sections.

Chromium(III) concentrations decreased from 1.6 mg L$^{-1}$ to <1 mg L$^{-1}$ after 25 d and to <50 µg L$^{-1}$ after 70 d, thus during the first days of the experiment the Cr(III) concentrations fluctuated heavily (Fig. 2d). It should be noted that variations may also arise from the fact that the determination of Cr(III) is made by the calculation of the difference of total Cr and Cr(VI), which are analyzed by different techniques, in different measuring ranges.

**Discussion**

**Dynamics of $E_{H}$, pH and Redox-Sensitive Species**

Watering of the soil columns induced decreasing $E_{H}$, as previously reported in other soil studies (Hindersmann et al., 2014; Hindersmann and Mansfeldt, 2014; Couture et al., 2015; Frohne et al., 2015). Reduction–oxidation reactions occur via electron transfer between electron acceptors and donors. Electrons are transferred under aerobic conditions, from reduced carbon to elemental O$_2$, which acts as the terminal electron acceptor. This process takes place with the involvement of microorganisms that gain energy from the mineralization of SOM. If soil pores are filled with water, the O$_2$ diffusion is extremely low, and microbial transformation processes rely on alternative terminal electron acceptors such as NO$_3^-$, Mn, Fe, and S (Zhi-Guang, 1985; Fiedler et al., 2007). This microbial reduction lowers the $E_{H}$ and reducing conditions develop. Therefore, reducing conditions are accompanied by proton-consuming processes (Bartlett and James, 1993), which are expressed by a simultaneously increasing pH and decreasing $E_{H}$ in our experiment. These redox-induced changes can be important because the pH influences the species distribution and mobility of Cr.

The redox-sensitive species NO$_3^-$, Mn, and Fe matched the dynamics of soil $E_{H}$ that were described by Mansfeldt (2004).
The results indicated that $\text{NO}_3^-$ was reduced to $\text{N}_2$, $\text{N}_2\text{O}$, or $\text{NH}_4^+$ under weakly reducing conditions ($E_h$ 100–300 mV), and nearly completely disappeared under moderately reducing conditions ($E_h < 100$ mV). As stated for $\text{NO}_3^-$, Mn oxides were also subsequently dissolved under weakly reducing conditions, and soluble Mn(II) was released into the soil solution. It is noticeable that the reduction of Mn oxides occurred in a staggered manner after the reduction of $\text{NO}_3^-$. As expected, Fe (hydr)oxides were reduced under moderately reducing conditions, although Fe concentrations in solution were altogether very low. Therefore, the amount of released Fe(II) was not limited by the total amount of Fe (hydr)oxides, which were present in excess, but rather results from a very slow dissolution of Fe (hydr)oxides, the precipitation of Fe as secondary mineral phases, or the adsorption of dissolved Fe. Liger et al. (1999) worked out that Fe(II) has a strong affinity for ferrihydrite and hematite at pH 7.5 to 8. Furthermore, the low content of SOM in the investigated soil may inhibits reduction of Fe (hydr)oxides. In general, organic carbon affects the amount of reducing substances either directly or indirectly, since it is the principal source of electrons in soils and can produce reducing substances during its decomposition (Chang-Pu and Zhi-Guang, 1985). During the first 20 to 30 d, Mn and Fe release was inhibited, which may have two reasons: (i) a certain time span is needed to reestablish facultative anaerobe and anaerobe microorganisms.

Fig. 2. Development of (a) $\text{NO}_3^-$ concentrations, (b) $\text{SO}_4^{2-}$ concentrations, (c) Cr(VI) concentrations, and (d) Cr(III) concentrations during the column experiment (black, column A; red, column B). Dashed lines indicate matrix potential changes.
after watering of soil (Rinklebe and Langer, 2006, 2008; Langer and Rinklebe, 2009); or (ii) the presence of high Cr(VI) concentrations inhibit the release of Mn and Fe, while the E$_{H}$, is controlled by CrO$_4^{2-}$/Cr$_2$O$_7^{2-}$ (s), or CrO$_4^{2-}$/Cu(II)OOH redox couples (Couture et al., 2015). Chromate/Cr(III) has a high standard electrode potential (Supplemental Table S1) and, thus, a high oxidation potential. Couture et al. (2015) hypothesized that the inhibition of Mn and Fe release is due to the scavenging of electrons by Cr, and therefore, no reduction of Fe or Mn oxides occurs in the presence of Cr(VI). However, the former one may be important during the first days of the experiment, but the latter for the period of the first 20 to 30 d, since the Mn and Fe release matched the point, in that the Cr(VI) concentration was constantly low.

During column drainage, NO$_3^-$ concentration increased quickly by nitrification, while dissolved Mn and Fe decreased by oxidation and precipitation of Mn and Fe oxides.

Although SO$_4^{2-}$ concentration decreased with decreasing E$_{H}$, a redox control of SO$_4^{2-}$ is unlikely given the measured E$_{H}$ (Supplemental Table S1). Dissimilatory SO$_4^{2-}$-reduction might be expected at strongly reducing conditions (Connell and Patrick, 1968) that were not achieved in our experiment. Furthermore, the largest decrease in SO$_4^{2-}$ concentration occurred at the beginning of the experiment, where E$_{H}$ was still high, and not at the stage of the experiment, where E$_{H}$ rapidly decreased. Apart from this, the release of SO$_4^{2-}$ at the beginning of the experiment is, in fact, a consequence of leaching processes of soluble or easy exchangeable SO$_4^{2-}$ that might be discharged from the COPR leachates.

**Chromium Speciation and Mobilization**

The results indicated a correlation between Cr behavior and E$_{H}$ values in the soil pore water. Chromium persists mainly in the environment as Cr(III) or Cr(VI), depending on pH and E$_{H}$ conditions (Fendorf, 1995). During the entire experiment, Cr(VI) was the dominant species. Under oxidizing conditions, Cr(VI) is normally the most thermodynamically stable oxidation state, and occurs mainly as CrO$_4^{2-}$ at pH >6.5, which is the pH range in this experiment. At pH <6.5, the protonated CrO$_4^{2-}$ species, HCrO$_4^-$, is also present in the surface environment (Hooda, 2010). However, we also detected Cr(III) in pore water during oxidizing, as well as moderately reducing conditions, although its concentration was very low compared to Cr(VI). Chromium (III) is the most stable form under reducing conditions, and is present as a cationic species, with the first Cr(OH)$_2^+$ or second Cr(OH)$_4^{2+}$ hydridolysis product in the pH range from 4 to 8 (Fendorf, 1995). The Cr(III) concentration in solution is certainly limited at pH >5, due to the formation of sparingly soluble amorphous Cr(III)-hydroxide (Cr(OH)$_3$), which is highly reactive with soil mineral surfaces, such as iron oxides (Rai et al., 1987; Hooda, 2010). Nevertheless, Cr(III) was also found in pore water at a pH >8. This is remarkable since potential soluble Cr(III) polynuclear species do not play an important role in aqueous solutions, and the low solubility of Cr(OH)$_3$ limits the Cr(III) concentrations between pH 6 and 12 (Rai et al., 1987).

Chromium(VI) concentration, in pore water samples collected at the beginning of the experiment, was very high, which arises from a large pool of readily available Cr under oxidizing and moderately oxidizing conditions. This point was also confirmed by the high percentage of the mobile and exchangeable fractions in the sequential extraction (Supplemental Table S2). It should be noted that Cr(VI) tends to bind strongly onto Fe oxides (Hsia et al., 1993; Abdel-Samad and Watson, 1997). Adsorption of Cr(VI) depends on pH and decreases with increasing pH (Jiang et al., 2008; Ajouyed et al., 2010). Thus, Cr(VI) is highly soluble under alkaline conditions, which was the case in this experiment. During the course of lowering E$_{H}$, Cr(VI) can be reduced to Cr(III) in the presence of reductants, such as organic material, Fe(II), and sulfides (Wittbrodt and Palmer, 1995; Zhihlin et al., 2004; Vodyanitskii, 2009). However, reduction of Cr(VI) by sulfides can be excluded, since the occurrence of sulfides in a predominantly oxic environment is unlikely. Furthermore, our soil contained only small amounts of SOM, which are not able to promote such high Cr(VI) reduction. Moreover, the reduction of Cr(VI) by SOM is slow with a half-life in the range of days or weeks (Zhihlin et al., 2004) and rate of reduction decrease with increasing pH (Wittbrodt and Palmer, 1995). In our experiment two different processes must be distinguished: (i) at the beginning (first 20 d) of the experiment, the decrease in Cr(VI) concentration may be at least a result of diluting effects, since the volume of the pore water samples were replaced by the uncontaminated monsoon solution; (ii) when E$_{H}$ drops and anoxia develops, Cr(VI) pore water concentrations decrease, due to reductive precipitation of Cr(VI) by Fe(II) (Lovley et al., 1996; Pollock et al., 2007; Whittleston et al., 2011). So, Cr(VI) is readily reduced by oxidation of Fe(II) and Cr(III) is likely incorporated into Fe(III) oxyhydroxides (Fendorf, 1995). This assumption is also confirmed by the low percentage of Fe in pore water under reducing conditions. The mixed Cr(III)–Fe(III) oxyhydroxide phase is resistant to air oxidation (Whittleston et al., 2011), which leads to an accumulation of Cr in this soil. This is also reflected in the high percentage of Cr bound onto Fe oxides. After soil drainage and returning to oxidizing conditions, only a small amount of Cr(VI) was remobilized. This minor remobilization may be attributed to either oxidation of Cr(III) or desorption of Cr(VI). Concerning naturally occurring oxidation of Cr in soils, O$_2$ and Mn oxides (e.g., birnessite) may act as an oxidant for Cr(III), whereby O$_2$ is known to be a very slow Cr(III) oxidant (Bartlett and James, 1979; Rai et al., 1989; Pettine and Capri, 2005). However, the content of Mn oxides is very low in the investigated soil, and any Mn oxides present would probably have been reduced under reducing conditions, although the course of Mn in pore water suggests that Mn oxides form rapidly under oxidizing conditions. Desorption of Cr(VI) is also promoted due to the alkaline milieu, and the high content of mobile and exchangeable Cr fraction.

Altogether Cr concentrations were higher under oxidizing conditions than under reducing conditions, which was also observed by Couture et al. (2015). However, Hidersmann and Mansfeldt (2014) observed an opposite trend in their microcosm experiment. They concluded that reductive dissolution of Fe oxides under moderately reducing conditions led to a release of Cr, which was reflected by strong correlation between the Cr concentration and dissolved Fe. Since Cr(III) is strongly retained by minerals at high pH or precipitates, they assumed that the dissolved Cr occurred as the oxidized species. Frohne et al. (2015) reported also an negatively correlation of Cr with E$_{H}$ due to adsorption of Cr on Fe (hydr)oxides at high E$_{H}$, and the release of Cr attributed to the reduction of Fe (hydr)oxides. The contrary results may arise from differences in soil composition.
and Cr species distribution. In our experiments, Cr(VI) was the dominant species under oxidizing conditions; in the experiments of Frohne et al. (2015), Cr(III) was considered to be dominant over the entire EₚH range. Furthermore, only 0.5% of the Cr was present in the mobile or easily mobilizable fraction in the experiments of Hindersmann and Mansfeldt (2014), which might be the reason for the low Cr concentration under oxidizing conditions. However, in our study 8.7% of the Cr was mobile or exchangeable, which provides a large pool of soluble Cr under oxidizing conditions. The high pH in our experiment additionally promotes the reductive precipitation of Cr under reducing soil conditions. Shaheen et al. (2014) figured out that Cr concentrations increased during long term flooding due to release of Cr bound to reductively dissolved Fe oxides or because of the indirect changes of pH caused by changes of EₚH. However, they also stated that a release of Cr even under aerobic/alkaline conditions can happen as well, which was the case in our experiment.

Within-Column Differences of EₚH and Cr Mobilization

There were no significant differences in the course of soil EₚH between the middle and lower column sections. However, the EₚH in the upper column section differed from the underlying column sections. A main reason could be that, during the course of the experiment, the soil surface slumped down and thus, the upper platinum electrode attained gradually oxidizing conditions, which is expressed by a slightly increasing EₚH. However, the measured species in pore water sampled from the upper suction cup indicate that this part of the column is, however, not located completely under oxidizing conditions. The pore water from the upper suction cup resembled those of the lower sections in pH, NO₃⁻, SO₄²⁻, Cr(III), and partly Cr(VI) concentrations. Hence, it is presumably that, except for the soil surface, the upper column section attains at least weakly reducing conditions during water saturation, where NO₃⁻ and Cr(VI) reduction occurs. It should be noted that even during the end of saturation no Mn and Fe were reduced, and the Cr(VI) concentration was not as low as in the underlying sections, so that the EₚH is probably in the upper range of moderately reducing conditions.

Influence of COPR Leachate on Cr Mobilization

Chromite ore processing residue leachate is characterized by high pH values and Cr(VI) concentrations (Matern and Mansfeldt, 2016). This Cr(VI) intake resulted in high percentages of mobile and exchangeable Cr in the soil and hence maximum Cr pore water concentrations of around 200 mg L⁻¹ under oxidizing conditions at the beginning of the experiment. Thus, the guideline value of Cr in groundwater that is set at a limit of 50 μg L⁻¹ by the World Health Organization (WHO, 2011) was exceeded by a factor of 4000. This is particularly alarming due to the predominance of the toxic Cr(VI). Furthermore, the alkaline milieu of the leachates generally prohibits Cr(VI) adsorption, especially in soils that only have a low acid buffer capacity (Matern and Mansfeldt, 2016). Moreover, the elevated Cr(VI) concentration in the pore water prevented the decrease of EₚH for a longer time, due to the scavenging of electrons, whereas the alkaline milieu of the COPR leachates led to precipitation of Cr(III) under moderately reducing soil conditions.

Beside Cr, high pore-water concentrations of NO₃⁻ and SO₄²⁻ at the beginning of the experiment also resulted from the COPR leachate intake, but normally do not influence Cr(VI) mobility in soils. The hyperalkaline Cr-contaminated soil-water system may also influence microbial communities, which play an important role in reductox processes. Whittleston et al. (2011) reported that, despite elevated pH and Cr(VI) concentrations, indigenous and adapted microorganisms exist, which are capable of Fe reduction. Furthermore, microbially mediated Cr(VI) reduction was also observed in other COPR-affected environments (Stewart et al., 2007, 2010).

Conclusion

This study showed that Cr(VI), derived from the COPR leachates, was highly mobile in the investigated soil under oxidizing conditions. Regarding the amounts of soluble Cr(VI), we expect a high discharge of Cr(VI) into the groundwater. With respect to the use of these soils as a cultivation area, the uptake of Cr(VI) by plants is also likely. On the other hand, Cr was effectively sequestered in the soil through the reductive precipitation of Cr(VI) by Fe(II), which can be an approach for remediation strategies. Nonetheless, the usage of this area for rice cultivation should be abandoned instantly, since the surface water is highly contaminated, even if Cr is present as insoluble Cr(III) in the underlying soil under water saturation.

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