Chromium contamination associated with Chromite Ore Processing Residue (COPR) in the area of Kanpur, Uttar Pradesh, India

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Summary

Chromite ore processing residue (COPR) is a hazardous waste derived from the chromate (CrO_4^{2-}) extraction roasting process. It is a major source of environmental contamination as it contains high amounts of chromium (Cr) in both the trivalent [Cr(III)] and the hexavalent [Cr(VI)] valence states. While Cr(III) is known to be an essential micronutrient for mammals, Cr(VI) is considered to be carcinogenic and causes allergic contact dermatitis. Despite its (eco)toxicological potential, COPR has been dumped in uncontrolled surface landfills in several countries. The leaching of Cr(VI), resulting in the contamination of groundwater, is a key environmental risk arising from these CORR dumps. Since the contamination pathways of Cr(VI) are not fully understood, the objective of this dissertation was to evaluate the Cr contamination associated with COPR in the area of Kanpur (Uttar Pradesh, India).

To investigate these issues, COPR samples were taken from two landfill sites in the area of Kanpur and characterized in terms of their chemical and mineralogical nature. The total Cr content in the studied COPR samples amounted to 81 and 74 g kg^{-1}, 20 and 13% of which was Cr(VI) respectively. In addition to the common mineral phases present in COPR, previously reported in other studies, a further Cr host mineral, grimaldiite [CrO(OH)], was identified by X-ray powder diffraction and scanning electron microscopy. Further, the COPR contained easily soluble phases such as sodium chromate (Na_2CrO_4). To determine the Cr(VI) leaching behavior of COPR, column experiments under water-saturated conditions were conducted. The results indicated that Cr(VI) concentrations in the leachates were dominated by the dissolution of Na_2CrO_4, as well as mineral solubility control of the Cr(VI) hosting minerals CAC-14 ($Ca_4Al_2O_6(CrO_4)\cdot 14H_2O$) and Katoite ($(CaO)_3Al_2O_3(H_2O)_6$). During leaching, Cr(VI) concentrations decreased from 1800 to 300 and 1200 to 163 mg L^{-1} during 12 pore volumes, which conforms to two years of monsoon precipitation. Furthermore, the release of Cr(VI) was partially rate-limited, which was identified by flow interruptions. Batch studies showed that CrO_4^{2-} adsorption from COPR eluates was inhibited due to the high pH of the eluates and the investigated soils. Furthermore, the chemical composition of the COPR eluates diminished CrO_4^{2-} adsorption due to their high ionic strength and carbonate concentration as a competitive anion. The Cr(VI) release from a COPR-contaminated soil at varying water content and redox conditions was studied using column experiments. Since Cr(VI) was present in high concentrations at the beginning of the experiment, the redox potential was controlled by $CrO_4^{2-}/Cr_2O_3(s)$ or CrO_4^{2-}/(Fe,Cr)OOH redox couples. The results indicated that Cr(VI) was highly mobile under oxidizing conditions and Cr was gradually immobilized and irreversibly sequestered via reductive precipitation under moderately reducing conditions. To evaluate the role of monsoon precipitation on Cr(VI) contamination of groundwater in the vicinity of COPR dumps, samples were taken both in the pre-monsoon season (n = 57) and during the monsoon season (n = 70). The

Cr(VI) concentrations of groundwater ranged from <0.005 to 115 mg L^{-1}, with the maximum values found close to the COPR dumpsites. Additionally, the results showed that most samples exhibited multiple non-COPR contaminates including fluoride, nitrate, arsenic, molybdenum, and uranium. Overall, the water from 95% of the wells was not drinkable. However, monsoon precipitation was not found to have a significant effect on Cr(VI) concentration and spatial distribution.

This study has shown that the area of Kanpur is highly affected by COPR dumps that continuously leach Cr(VI) in high concentrations. Hexavalent Cr is not adsorbed by the soils in the surroundings, which is reflected in the elevated Cr(VI) concentrations in the groundwater around the dumpsites. This is particularly alarming since the local population uses the groundwater not only to water livestock and for irrigation but also as drinking water. The use of permeable reactive barriers (either as a stand-alone remediation process or in conjunction with the capping of the COPR dumpsites) is a cost effective and practical solution to counteract the negative effects of Cr(VI) pollution. Furthermore, Cr-mitigation at the household level should be provided.

Zusammenfassung

Chromerzverarbeitungsrückstände, die im Englischen als Chromite Ore Processing Residue (COPR) bezeichnet werden, sind umweltgefährliche Abfälle, die aus dem Röstungsprozess zur Chromat (CrO_4^{2-}) Extraktion stammen. Sie sind eine bedeutende Quelle für Umweltverschmutzungen, da sie große Mengen an Chrom (Cr), sowohl im drei- [Cr(III)] als auch im sechswertigen [Cr(VI)] Valenzzustand enthalten. Obwohl Cr(III) bekanntlich ein Mikronährelement für Säugetiere darstellt, wird Cr(VI) als karzinogen eingestuft und verursacht allergische Kontaktekzeme. In einigen Ländern wurden COPR aber trotz ihres (öko)toxikologischen Gefährdungspotentials in unkontrollierten Oberflächenhalden abgelagert. Eine große Gefahr, die von den COPR-Halden ausgeht, ist die Auswaschung von Cr(VI) und die damit verbundene Kontamination des Grundwassers. Da die Pfade der Cr(VI) Kontamination nicht vollständig geklärt sind, war das Ziel dieser Dissertation daher die Cr-Kontamination in Verbindung mit COPR in dem Gebiet um Kanpur (Uttar Pradesh, Indien) zu beurteilen.

Um diesen Sachverhalt zu untersuchen, wurden COPR Proben von zwei Halden in der Region von Kanpur genommen und im Hinblick auf ihre chemische und mineralogische Zusammensetzung hin untersucht. Der Gesamtchromgehalt betrug 81 und 74 g kg^{-1}, wovon 20 bzw. 13% als Cr(VI) vorlagen. Abgesehen von den gängigen Mineralphasen, die in den COPR in anderen Studien benannt wurden, konnte ein weiteres Mineral, Grimaldiit [CrO(OH)], mittels Röntgenbeugung und Rasterelektronenmikroskopie identifiziert werden. Des Weiteren enthielten die COPR leicht lösliche Phasen wie Natriumchromat (Na_2CrO_4). Um das Auslaugverhalten von Cr(VI) in COPR zu untersuchen, wurden Säulenversuche bei gesättigtem Fluss durchgeführt. Die Ergebnisse lassen darauf schließen, dass die Auflösung von Na_2CrO_4, sowie die Löslichkeitskontrolle von den Cr(VI) enthaltenden Mineralphasen CAC-14 ($Ca_4Al_2O_6(CrO_4)\cdot 14H_2O$) und Katoite ($(CaO)_3Al_2O_3(H_2O)_6$) für die Cr(VI) Konzentration in dem Sickerwasser verantwortlich waren. Während der Auslaugung, verringerten sich die Cr(VI) Konzentrationen von 1800 auf 300 mg L^{-1} und 1200 auf 163 mg L^{-1} innerhalb von 12 Porenvolumen, was zwei Jahren Monsunniederschlag entspricht. Flussunterbrechungen ergaben, dass die Freisetzung von Cr(VI) teilweise ratenlimitiert war. Schüttelexperimente zeigten, dass die Adsorption von CrO_4^{2-} in den COPR-Eluaten aufgrund der hohen pH-Werte von Böden und Eluaten gehemmt war. Außerdem führte die chemische Zusammensetzung der COPR-Eluate aufgrund ihrer hohen Leitfähigkeit und Anzahl an konkurrierenden Anionen (v.a. Carbonationen) zu einer verringerten Adsorption. Die Freisetzung von Cr(VI) in einem COPR-kontaminierten Boden wurde in Abhängigkeit variierender Wassergehalte und Redoxpotenziale in Säulenexperimenten untersucht. Durch die hohe Cr(VI) Konzentration zu Beginn des Experimentes, wurde das Redoxpotenzial durch die Redoxpaare $CrO_4^{2-}/Cr_2O_3(s)$ oder CrO_4^{2-}/(Fe,Cr)OOH kontrolliert. Die Ergebnisse zeigten auch, dass Cr(VI) unter oxidierenden Bedingungen sehr mobil war, unter moderat reduzierenden Bedingungen schrittweise immobilisiert und irreversibel durch reduktive Fällung abgesondert wurde. Um die Abhängigkeit von Monsunniederschlägen auf die Cr(VI) Kontamination im Grundwasser in der Umgebung der COPR-Halden zu untersuchen, wurden Proben vor Monsunbeginn (n = 57) und während des Monsuns (n = 70) genommen. Die Cr(VI)-Konzentrationen reichten von <0.005 bis 115 mg L^{-1} und erreichten Maximalwerten in der Nähe der COPR-Halden. Zusätzlich ergaben die Ergebnisse, dass die meisten Proben mehrfach mit Fluorid, Nitrat, Arsen, Molybdän und Uran kontaminiert waren, was allerdings nicht in den Zusammenhang mit den COPR Halden gebracht werden konnte. Insgesamt war das Wasser von 95% der Brunnen nicht trinkbar. Allerdings konnte kein Zusammenhang zwischen Monsunniederschlägen und der räumlichen Verteilung der Cr(VI) Konzentration im Grundwasser festgestellt werden.

Die Studie hat gezeigt, dass die Gegend um Kanpur durch die COPR-Halden, aus denen kontinuierlich Cr(VI) ausgewaschen wird, sehr beeinträchtigt ist. Das sechswertige Cr wird in den umgebenden Böden kaum gebunden, was sich in erhöhten Cr(VI) Grundwasserkonzentrationen widerspiegelt. Das ist besonders bedenklich, da die ansässige Bevölkerung das Grundwasser nicht nur für die Tränkung der Tiere und für die Bewässerung der Ackerflächen benötigt, sondern auch als Trinkwasser nutzt. Die Verwendung einer permeablen reaktiven Barriere (entweder alleine oder in Kombination mit der Überdachung der COPR Halden) bietet eine kostengünstige und praktikable Lösung, um den negativen Folgen der Cr(VI) Verschmutzung entgegen zu wirken. Außerdem sollte zumindest eine Minderung des Cr-Schadens auf Haushaltsebene bereitgestellt werden.

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Contents

Chapter 1 Introduction

Introduction

Leather is one of the most widespread commodities in the world. The estimated global trade value amounts to approximately 100 billion US$ per year (UNIDO, 2010). Hence, the leather industry plays an important role in the world's industry. In 2013, heavy leather production totaled $567 \cdot 10^3$ megagram (Mg), while 1.29 billion square meter of light leather, including split leather, were produced (FAO, 2015). Since the middle of the last century, the labor-intensive and most highly polluting parts of the leather industry have been stepwise moved from the developed world to developing and countries with emerging economies. China has been, by far, the most significant player in all sectors of the leather industry in the recent years, followed by Brazil, Italy, Russia, and India (FAO, 2015; UNIDO, 2010).

Nowadays, the leather industry is an important part of the Indian industry. Current estimates of the Indian Government indicate that around 2.5 million workers are employed in the Indian leather industry (Bose et al., 2012). The export of leather and leather products for the financial year April-March 2014 – 2015 amounted to 6.5 billion US$ (CLE, 2015). About 20% of the leather is exported, the other 80% are processed further, especially to footwear (35%, 2.28 billion US$) and footwear components (5.6% 0.36 billion US$) (CLE, 2015). The major markets for Indian leather and leather products are Germany with a share of 12.3%, the US with 11.8%, the U.K. with 11.6%, and Italy with 7.8% (CLE, 2015).

One major agglomeration of the Indian tannery industry is placed in the Kanpur area in the state of Uttar Pradesh, North India. The center of the leather industry in Kanpur is constituted of about 450 tanneries (Srinivasa Gowd et al., 2010). Beside the high number of tanneries in Kanpur, several basic chromium sulfate (BCS) producing factories are residing in small villages in the surrounding area. The BCS is used as a tanning agent in the conventional leather tanning process and is produced by the chromate (CrO_4^{2-}) extraction roasting process. For the last 100 years, the conventional chrome (Cr) tanning has been the dominant method of making leather. However, the residues of the tanning process and its upstream supplier sector are highly contaminated by Cr and other pollutants. As a consequence, non-chrome tanning methods, for example the use of vegetable tanning of leather, have become quite popular, especially in automobile manufactures. Nevertheless, Basford (2008) and Germann (2008) assumed that over the next decades or longer, Cr tanning will remain the main process for leather production carried out in the world. Thus, enormous environmental problems are the consequence of this polluting leather tanning industry.

Chromite ore processing residue – Generation, properties and environmental effects

Chromite ores are the exclusive feedstock for the commercial production of the several Cr compounds in use. The mineral has a spinel structure with the general formula AB_2O_4 in which A is a divalent cation (Fe, Mg), and B is a trivalent cation (Cr, Fe, Al) (Tathavadkar et al., 2004). Thus, the overall formula of this mineral can be expressed by $(Mg,Fe)(Al,Cr,Fe)_2O_4$. Tathavadkar et al. (2004) investigated eight chromite ore samples from South Africa, India, Philippines, China, and Indonesia and found Cr contents between 30% and 35% by weight.

Basic chromium sulfate is a widely used tanning agent in the leather tanning industry. It is therefore a challenge for the Cr chemical industry, to convert the containing Cr from the relatively unreactive ore in a soluble form. The process used in the industry is based on high temperature alkaline oxidation. The initial stage of the process is the conversion of insoluble chromite ore into water-soluble CrO_4^{2-}. Therefore, chromite ore is mixed with sodium carbonate and lime and roasted at 1,100 °C for 45 minutes, which produces sodium chromate (Na_2CrO_4) (equation 1). Lime, limestone, or dolomite are added during the roasting process to act as a mechanical separator allowing oxygen to react with the chromite and sodium carbonate and as a sequestering agent combining with various ore impurities (Tathavadkar et al., 2001). The Na_2CrO_4 produced is extracted in water, and the residue, the so called chromite ore processing residue (COPR), is discarded.

$$4(Fe,Mg)Cr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2 \quad [1]$$

Sodium chromate is then converted into sodium dichromate by reaction with sulfuric acid. Narrowing and heating lead to crystalline dichromate, which is subsequently pounded (equation 2).

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O \quad [2]$$

The addition of molasses and the following reduction of $Na_2Cr_2O_7$ lead to the formation of BCS (equation 3).

$$8Na_2Cr_2O_7 + H_2SO_4 + C_{12}H_{22}O_{11} \rightarrow 16Cr(OH)SO_4 + 8Na_2SO_4 + 22H_2O + 12CO_2 \quad [3]$$

The production process was introduced in 1845 and was the primary commercial method of Cr production up to the 1960s (Darrie, 2001). As a disadvantage, the process is inefficient as producing large quantities of COPR waste. Millions of tons of COPR have been discarded worldwide due to the process (Darrie, 2001). Historically, COPR was disposed of in some urban areas such as Glasgow, Scotland, UK, and Hudson County, New Jersey, USA. In Glasgow, COPR was generated by Cr chemical works during the period 1830 to 1968 (Farmer et al., 2006; Graham et al., 2006). While the last deposition of COPR is over 40 years ago, Cr(VI) is still leaching out in large quantities. Three high-lime chromite ore processing plants located in Hudson County operated between 1905 and 1971 and produced over 2 million tons of COPR that were historically deposited in over 160 sites (Chrysochoou et al., 2010). Nowadays, most of the developed countries have abandoned the high lime process or use lime-free technologies, which are a much safer production method (Tathavadkar et al., 2001). However, the high-lime Cr extraction is still being used in China, Russia, Kazakhstan, Pakistan, and India, which recently accounted for 40% of Cr production worldwide (Darrie 2001). Darrie (2001) estimated that high-lime process plants generate about 600,000 Mg yr^{-1} of COPR.

In general, COPR contains unreacted chromite ore as well as unextracted CrO_4^{2-}. The material is highly alkaline with pH values varying from 11 to 12.5, as it contains a high amount of lime (Chrysochoou et al., 2009a; Deakin et al., 2001; Földi et al., 2013). Residual Cr contents of COPR range from 20 to 110 g kg^{-1} (Farmer et al., 1999; Földi et al., 2013; Geelhoed et al., 2003), of which up to 30% is present as Cr(VI) (Geelhoed et al., 2003). From a mineralogical point of view, minerals and compounds identified in COPR can be divided into three groups according to Hillier et al. (2003): i) non-reacted feedstock ore, ii) high temperature phases produced during Cr extraction, and iii) minerals formed under ambient weathering conditions on the disposal sites (Table 1.1). Post depositional mineral transformations mainly result from hydration and absorption of atmospheric CO_2, which is favored due to the high alkalinity of the material.

Table 1.1 Minerals identified in COPR samples using X-ray powder diffraction and known Cr substitutions (Hillier et al., 2003), modified.

Group	Mineral	Chemical formula	Cr substitutions
I	chromite	$(Fe,Mg)Cr_2O_4$	
II	brownmillerite	$Ca_2(Al,Fe,Cr)_2O_5$	Cr^{3+} for Fe, Al
	larnite	Ca_2SiO_4	
	periclase	MgO	
	portlandite	$Ca(OH)_2$	
III	aragonite	$CaCO_3$	
	brucite	$Mg(OH)_2$	
	calcite	$CaCO_3$	
	ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$	CrO_4^{2-} for SO_4^{2-}
	hydrocalumite	$Ca_2(Al,Fe)(OH)_6(OH)\cdot 3H_2O$	Cr^{3+} for Al, Fe, CrO_4^{2-} as the anion
	hydrogarnet	$Ca_3(Al,Fe)_2(H_4O_4)_3$	Cr^{3+} for Al, Fe,
	sjogrenite	$(Mg_6Fe_2(OH)_{16})(CO_3)(H_2O)_4$	CrO_4^{2-} as the anion

Apart from chromite, Cr occurs in brownmillerite, hydrocalumite, and hydrogarnet as Cr^{3+} substitutes for Al and Fe. Moreover, in ettringite CrO_4^{2-} is substituted for SO_4^{2-}. Hillier et al. (2007) observed up to 50% CrO_4^{2-} substitution in ettringite crystals in Glasgow COPR. Furthermore, Chrysochoou et al. (2009a) demonstrated that layered double hydroxides like hydrocalumite might play an important role in the sequestering of Cr(VI) in COPR because of their anion exchange properties, in which CrO_4^{2-} is substituted for OH^-. Hillier et al. (2007) emphasized the exceptional importance of hydrogarnet as a Cr(VI)-host phase in COPR, in which up to 50% of the total Cr(VI) was recorded. According to Chrysochoou and Dermatas (2007) it is also possible that sjogrenite retains CrO_4^{2-} in the interlayer, apart from carbonate and/or hydroxyl. It is controversially discussed, whether brucite and portlandite can bind Cr(VI), but Ginder-Vogel et al. (2005) found that Cr(III) and Cr(VI) were associated with portlandite grains. After deposition, COPR is not stable and undergoes weathering reactions, where dissolution of Cr(VI)-bearing minerals is the main process being responsible for the release of Cr(VI) (Chrysochoou et al., 2010; Geelhoed et al., 2002; Geelhoed et al., 2001). As a consequence, contamination of groundwater is a key environmental risk arising at COPR sites. Concentrations up to 91 and 6.7 mg L^{-1} Cr(VI) have been measured in Scottish COPR-affected groundwater and tributary stream, respectively (Farmer et al., 2002). Burke et al. (1991) detected Cr(VI) concentrations up to 30 mg L^{-1} in groundwater samples in New Jersey COPR-affected areas. As deduced from batch experiments, not adsorption and desorption but dissolution and precipitation processes are governing the solubility of Cr(VI) in COPR at inherent pH. Possible solubility controlling minerals are hydrogarnet, hydrocalumite, and ettringite (Geelhoed et al. 2002, Wazne et al. 2008).

Biogeochemistry of chromium in the terrestrial environment

Chromium is an omnipresent and redox sensitive transition metal in the environment. Altogether, Cr is abundant in the earth crust with contents ranging from 80 to 200 mg kg^{-1} (Adriano, 2001). The Cr content of uncontaminated soils is largely determined by the parent material and ranges from 5 to 1,500 mg kg^{-1}, with an average content of 70 mg kg^{-1} (Essington, 2004). In nature, the most common oxidation states of Cr are +III, Cr(III), and +VI, Cr(VI). Thereby the oxidation state controls its chemical properties and environmental behavior as well as the effect on organisms. According to today’s knowledge, Cr(III) is essential for mammals for the maintenance of normal carbohydrate, lipid, and protein metabolism (Pechova and Pavlata, 2007). On the contrary, Cr(VI) is known to be a potent carcinogen and extremely toxic. Numerous epidemiological studies have reported the relation between lung cancer and inhalation exposure to Cr(VI) (Halasova et al., 2009; Holmes et al., 2008). Furthermore, Cr(VI) has also a carcinogenic potential by oral exposure (Sun et al., 2015), for example, when consumed from drinking water (Sedman et al., 2006), although most of the Cr(VI) is extracellular reduced to

Cr(III) in the gastrointestinal system. Repeated exposure of Cr(VI) can also cause allergic contact dermatitis and skin ulcers (Shelnutt et al., 2007). Moreover, Cr compounds are also highly toxic to plants and are detrimental to their growth and development (Nagajyoti et al., 2010).

The fate and chemical behavior of Cr in soils depend on pH, redox potential, presence of electron donors and acceptors, oxidation state, soil compounds, competing ions, and complexing agents (Adriano, 2001). Hydrolysis of the aqueous dissolved Cr(III) cation, $Cr(H_2O)_6^{3+}$, results in the formation of different mononuclear hydroxo species: positively charged species, mainly $Cr(OH)^{2+}$, dominate at pH values from 3.8 to 6.3, the neutral species, $Cr(OH)_3^0$, at pH values from 6.3 to 11.5, and the negatively charged species, $Cr(OH)_4^-$, at pH values > 11.5 (Rai et al., 1987). The formation of polynuclear species such as $Cr_2(OH)_2^{4+}$ + and $Cr_3(OH)_4^{5+}$ is unlikely at the expected low Cr concentrations in the environment (Rai et al., 1987). Aqueous dissolved Cr(VI) is exclusively present in anionic form with $HCrO_4^-$ being predominant at pH < 6.5, and CrO_4^{2-} predominant at pH > 6.5 (Fendorf, 1995). Polynuclear species such as $HCr_2O_7^-$ and CrO_7^{2-} are also unlikely in the environment, since their formation requires Cr(VI) concentrations $> 10^{-2.1}$ M (Baes and Mesmer, 1976).

Both, Cr(III) and Cr(VI), interact with the surfaces of minerals by adsorption. Trivalent Cr is rapidly and specifically adsorbed by Fe and Mn oxides as well as organic matter, where adsorption depends on pH and increases with increasing pH (Anmacher, 1981; Bartlett and Kimble, 1976). Chromium(III) is also retained by clay minerals such as kaolinite and montmorillonite (Griffin et al., 1977). Griffin et al. (1977) found that Cr(III) adsorption increased with increasing pH due to cation exchange reactions of the hydrolyzed species. Additionally, at pH values > 5.5, Cr(III) precipitates as a sparingly soluble amorphous Cr(III)-hydroxide, which is highly reactive with soil mineral surfaces such as iron oxides. Only if complexed with organic acids, such as citric acid or fulvic acid, Cr(III) can remain soluble at pH values up to 6.7 or higher depending on pK_a and concentrations of complexing ligands (James and Bartlett, 1983a).

Numerous studies have investigated the adsorption of CrO_4^{2-} with different soil components as a function of initial concentration, pH, ionic strength, and competing anions (Abdel-Samad and Watson, 1997; Aide and Cummings, 1997; Ainsworth et al., 1989; Ajouyed et al., 2010; Fendorf et al., 1997; Garman et al., 2004; Grossl et al., 1997; Hsia et al., 1993; Jiang et al., 2012; Mesuere and Fish, 1992b; Zachara et al., 1987). Chromate, being an anion, is adsorbed by various mechanisms onto hydrous oxides of Al and Fe that are main constituents in soils and commonly have a net positive charge as well as a potential chemical affinity for CrO_4^{2-} (Fendorf, 1995). Spectroscopic analysis indicated that CrO_4^{2-} was adsorbed via ligand exchange with surface hydroxyl groups resulting in the formation of inner-sphere surface complexes (Fendorf et al., 1997; Hsia et al., 1993; Jiang et al., 2008). Modelling studies suggested that CrO_4^{2-} is also retained via electrostatic adsorption and the formation of outer-sphere surface complexes (Ainsworth et al., 1989; Benjamin and Bloom, 1981; Zachara et al., 1989; Zachara et al., 1987). Moreover, Zachara et al. (1988) observed the formation of weak surface complexes between CrO_4^{2-} and kaolinite. The extent of CrO_4^{2-} adsorption is highly determined by pH and decreases with increasing pH (Ajouyed et al., 2010; Jiang et al., 2008). Furthermore, the adsorption maximum is expected to be at pH values close to the pK_{a1} of the conjugated acid, chromic acid, which is very low ($pK_{a1} = -0.2$; Martell et al. (2004)). Chromate adsorption is also affected by various oxoanions (e.g. PO_4^{3-}, CO_3^{2-} and, SO_4^{2-}), which compete for binding sites either directly or indirectly by reducing positive charge, and thus, significantly reduce the amount of adsorbed CrO_4^{2-} (Aide and Cummings, 1997; Villalobos et al., 2001; Zachara et al., 1987).

Overall, the low solubility of Cr(III)-hydroxide ($Cr(OH)_3$, $pK_s = 9.35$) and the strong adsorption onto soil constituents at pH > 5.0 result in a low mobility and bioavailability of Cr(III) in soils (Avudainayagam et al., 2003; Fendorf, 1995; Ma and Hooda, 2010). In contrast, Cr(VI) is highly mobile, particularly under slightly acid to alkaline conditions (Fendorf, 1995).

Oxidation-reduction reactions can convert Cr(III) to Cr(VI) and vice versa (Adriano, 2001). In the presence of organic substances, Fe(II), and sulfides, Cr(VI) can be reduced to Cr(III) (Fendorf, 1995). However, the reduction of Cr(VI) by organic substances is slow with a half-life time in the range of days or weeks (Zhilin et al., 2004). Furthermore, the rate of reduction is strongly pH-dependent and increases with decreasing pH (Wittbrodt and Palmer, 1995). However, James and Bartlett (1983b) noted that Cr-organic complexes did form when Cr(VI) was reduced by soil organic material and the resulting complexes may interact with manganese oxides (James and Bartlett, 1983a), which leads to the reoccurrence of Cr(VI) in soil or water. By contrast, the reduction of Cr(VI) by Fe(II) leads to the formation of $Fe,Cr(OH)_3$ solids with low solubility, which diminish the potential for re-oxidation (Fendorf, 1995). Since the reaction is rapid, Cr(VI) reduction by Fe(II) can even occur in aerated soils (Eary and Rai, 1989). Iron sulfides (FeS or FeS_2), which are prevalent in anoxic environments, have also a significant influence on Cr(VI) reduction (Fendorf, 1995). The reduction reaction is pH-dependent, with reduction increasing with decreasing pH. Thus, Cr(VI) reduction in soils is inhibited under alkaline conditions (James, 1994; Zhilin et al., 2004). The directly transformation from Cr(VI) to Cr(III) under reducing conditions does not commonly occur, due to kinetic limitations based on electron symmetry constraints in the electron transfer (Fendorf, 1995). However, some bacteria are also able to reduce Cr(VI) to Cr(III) under aerobic (Bopp and Ehrlich, 1988; Christl et al., 2012; Garbisu et al., 1998; Xu et al., 2015) or anaerobic conditions (Thatoi et al., 2014; Wang et al., 1989).

Concerning naturally occurring oxidation of Cr in soils, oxygen and manganese oxides (e.g., birnessite), may act as an oxidant for Cr(III). However, dissolved oxygen can only oxidize small amounts of Cr(III) at pH values above 9, but not at pH values normally occurring in most soils (Bartlett and James, 1979). Furthermore, the oxidation of Cr(III) by dissolved oxygen has been reported to be very slow (Rai et al., 1989; Schroeder and Lee, 1975). Eary and Rai (1987) reported that no Cr(III) reduction occurred in a 19 µM Cr(III) solution with approximately 8 mg L^{-1} dissolved oxygen at pH values ranging from 4 to 12.5 even after 24 days. Therefore, manganese oxides are likely to be the more important oxidants for Cr(III) in soils and groundwater systems (Eary and Rai, 1987). However, the reaction is controlled by many factors, such as the surface characteristics of oxides, competitive ions, pH and the availability of dissolved Cr(III) to the surface of manganese oxides (Apte et al., 2006; Eary and Rai, 1987). Dai et al. (2009) reported that lower pH and higher concentration of manganese oxide markedly enhance the rate and extent of aqueous Cr(III) oxidation. Feng et al. (2006) found out that oxidation of Cr(III) by the manganese oxide minerals was, or tended to be, an equilibrium reaction and was controlled thermodynamically when pH was below 5.0. When pH was above 5.0 to 5.5 $Cr(OH)_3$ precipitate resulting in a lower pH effect on Cr(III) oxidation.

The chromium pollution situation in the region of Kanpur, India

Kanpur is one of the highly industrialized cities in northern India. Almost 800 industries are involved in manufacturing various products (Dwivedi et al., 2015). An important branch of industry is the leather processing clusters of tanning industry, in which Kanpur is a prominent center for. Wastes from these tanneries and related industries have polluted plants, soils, sediments, rivers, and ground waters of the surrounding Ganga plain (Ansari et al., 1999; Singh et al., 2009; Sinha et al., 2006; Srinivasa Gowd et al., 2007; Srinivasa Gowd et al., 2010). It is estimated that in India alone, tanning industries alone release about 2,000 to 3,200 Mg of Cr (basis is elemental Cr) into the environment annually (Apte et al., 2005; Kumar and Riyazuddin, 2010). Singh et al. (2014) investigated 165 groundwater samples in Kanpur and found maximum Cr concentration of 3.2 mg L^{-1}, with a mean value of 0.06 mg L^{-1}. Analyses of groundwater samples by Singh et al. (2009) revealed concentrations of up to 16.3 mg L^{-1} Cr(VI) for the region of Kanpur largely exceeding the national threshold of 0.05 mg L^{-1} for total Cr. Srinivasa Gowd et al. (2010) examined soils in and around Kanpur and found Cr values ranging from 162 to 6,228 mg kg^{-1} with a mean value of 2,652 mg kg^{-1}.

Basic chromium(III) sulfate ($Cr(OH)SO_4$) plays a central role in the tanning of leather, since Cr(III) give polychromium(III) compounds that are active in tanning, being the cross-linking of the collagen subunits (Covington, 1997). To satisfy the local demand for Cr(III) salts in Kanpur, Cr works have been established in the suburbs Rania and in Chhiwali in the late 1980s and 2004, respectively. The COPR from the production of BCS has been illegally disposed of in the surroundings of the factories. Singh et al. (2012) investigated 27 soils in Rania and found Cr contents ranging from 26 to 236 mg kg^{-1} with a mean content of 64.4 mg kg^{-1}, from which five samples showed significant presence of Cr(VI) with an average value of 15.8 mg kg^{-1}. Földi et al. (2013) examined 21 samples in the area of Kanpur and found Cr contents ranging from 0.06 to 109 g kg^{-1}, from which six samples were identified as highly Cr contaminated COPR. Moreover, leaching of Cr(VI) from COPR sites in Rania is evident from the strong yellow colour of well water. Field test-kits indicated Cr(VI) concentrations of up to 80 mg L^{-1} in piezometers close to the main dumpsite in Rania (Singh et al., 2013). Charan et al. (2010) investigated 21 water samples in the same area and found Cr concentration up to a maximum of 42.5 mg L^{-1}.

Outline of this thesis

As outlined above, the Cr pollution situation in the area of Kanpur is alarming, especially in the vicinity of BCS works located in Rania and Chhiwali. Starting from the introducing review, the project addresses the following issues:

Obviously, illegally dumped COPR is the major source of Cr(VI) groundwater contamination in this area, resulting in severe health consequences for the local population, since they use the water for drinking, cooking, washing, watering of live-stock, and irrigation. The outline of this thesis was hence to study the Cr contamination pathways associated with COPR from the deposited waste right up to the influx into the groundwater (Fig. 1.1). In this respect, the mineralogical composition and solid-state speciation of Cr in COPR (Fig. 1.1, point 1) as well as the Cr(VI) leaching behavior (Fig. 1.1, point 2) were in the focus. Regarding the interaction between the COPR leachate and the soil solid phase, CrO_4^{2-} adsorption (Fig. 1.1, point 3) and reduction–oxidation reactions (Fig. 1.1, point 4) were of particular interest. Finally, the environmental effect, reflected in groundwater contamination, was investigated (Fig. 1.1, point 5).

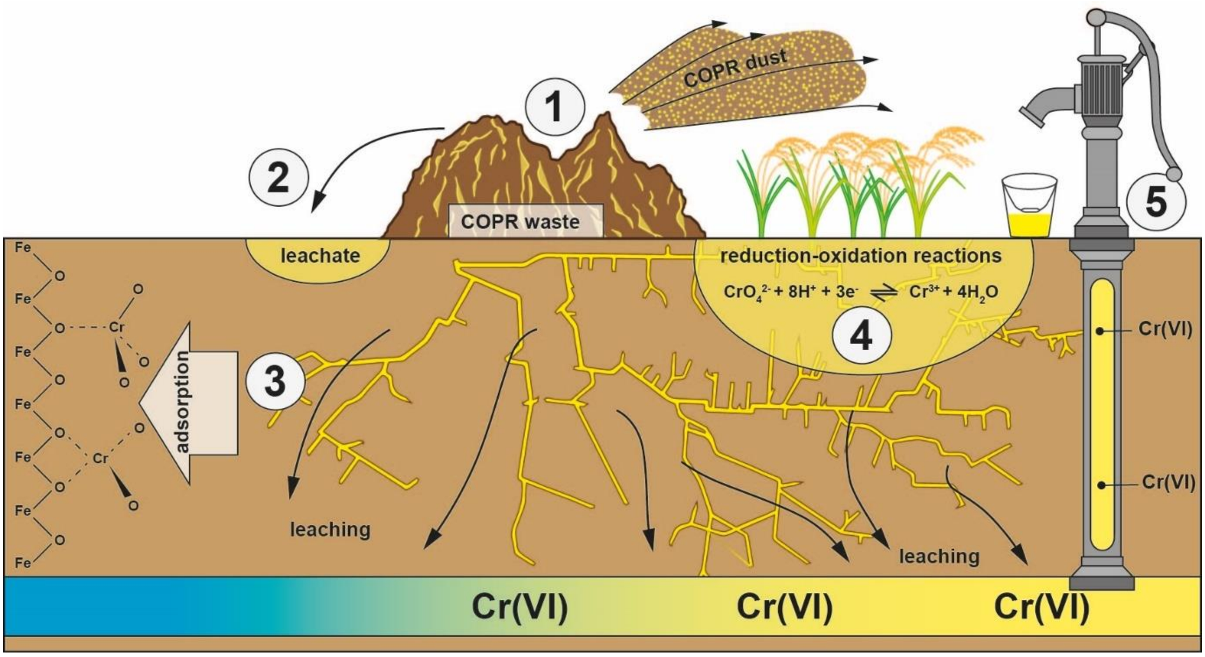


Fig. 1.1 Chromium contamination pathways associated with COPR.

Although the mineralogy and solid-state speciation of Cr in COPR deposits have been studied in the USA and Europe, the present findings of investigation cannot be simply transposed to the Indian sites, since COPR originating from various locations may differ with regard to its mineralogy and leaching behavior due to differences in chromite ore composition and extraction process. Furthermore, the deposition practice may vary, since COPR is often mixed with indigenous soil at some deposition sites, whereas it is dumped as pure COPR at other sites. Even dumped as pure COPR, the approach of deposition may effect COPR composition due to sorting of grain size and varying available contact surface for weathering. Another point are the outstanding ambient weathering conditions. Previous studies have investigated COPR from sites located in the temperate zone. The Indian sites, however, are in the humid subtropical climate zone with dry winter season. Additionally, the precipitation pattern is completely different since ~80% of the annual rainfall occurs during the three-month monsoon period. In consequence, moisture of deposited COPR should strongly vary from dry to wet which, in turn, affects hydration and CO_2 absorption. Finally, the factor time is different because the Indian COPR are relatively young (< 25 yr) compared to the Glasgow and North American COPR (between at least 40 and 180 yr). Consequently, the mineralogical composition and resulting leaching behavior may be different at the Indian sites in comparison to other COPR sites investigated before. Hence, there is a general need to study the release of Cr(VI) from this unknown matrix at realistic conditions, i.e., considering monsoon precipitation with tropical heavy-rain events and with effects on varying moisture and redox conditions in contaminated soils. Assessing the rate of release of Cr(VI) from contaminated material, however, is essential for the evaluation of environmental risks.

Concerning Cr contamination of arable land, published surveys have shown that many soils in the area of Kanpur are heavily affected as indicated by elevated total Cr concentrations (Srinivasa Gowd and Reddy, 2010). However, information on both distribution and speciation of Cr as well as adsorption behavior in the affected soils is lacking. In case of Cr, the speciation is of uppermost importance as toxicity is linked to Cr speciation. The combined detailed investigation of Cr distribution and speciation in polluted soils will reveal prevalent Cr reduction and transport pathways. This knowledge is required for proposing adequate measures to counteract negative effects of Cr(VI) pollution.

Altogether, the identification of similarities and differences between the Indian COPR and COPR dumped in other countries may be helpful, to understand transformation processes on site and at least, to implement new remediation strategies or to modify existing remediation strategies for the Indian sites.

To investigate these issues, the following preliminary hypotheses were formed and addressed in the course of this thesis:

Hypothesis 1 – *The COPR material from the Indian sites differs in its mineralogy and Cr content from COPR material obtained from Europe and the USA.*

Hypothesis 2 – *Mineralogical composition significantly influences the leaching of Cr(VI) from COPR.*

Hypothesis 3 – *COPR leachate composition influences the CrO_4^{2-} adsorption behavior of soils.*

Hypothesis 4 – *Cr(VI) release from COPR-contaminated soil is influenced by varying water content and redox conditions.*

Hypothesis 5 – *Groundwater is highly contaminated with Cr(VI) in the surroundings of the COPR dumpsites.*

Hypothesis 6 – *Monsoon precipitation drives the influx of Cr(VI) from the COPR dumpsites into the groundwater resulting in elevated Cr(VI) concentrations.*

Research design and applied methods

To verify or falsify the formed hypotheses microscopic and macroscopic experimental techniques were coupled to identify the solid phases and the rates and mechanisms of Cr dynamics in COPR wastes as well as in Cr-polluted soil.

At the beginning of the project, COPR samples, selected on the basis of information given by the Indian nongovernmental organization Ecofriends (President Mr. R. Jaiswal), were taken at two abandoned, illegally operating disposal sites in the area of Kanpur, North India (*Chapter 2*). The samples were analyzed with X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), and various digestion and extraction methods, complemented by other laboratory methods. The results allow the identification of the mineralogical and chemical characteristics of the COPR samples and are presented in *Chapter 3*. In *Chapter 4*, the release of Cr(VI) from COPR was studied with the column flow technique. The distinct hydrologic conditions induced by monsoon events were thereby considered. Geochemical modeling was used to identify potential mineral phases controlling Cr(VI) leaching. *Chapter 5* focused on the adsorption behavior of CrO_4^{2-} in soils. This issue was investigated with COPR leachates in a batch technique. Afterwards, in *Chapter 6*, the assessment of Cr(VI) release from a contaminated soil, affected by hyperalkaline leachates from COPR was investigated in a column experiment, with the effects of water contents and redox conditions on Cr(VI) mobilization being of special concern.

The objectives of the last part of the project were (i) to identify the COPR waste sites in three industrial areas, (ii) to investigate the geochemical characteristics of groundwater in the surroundings of the COPR sites, (iii) to asses and classify the groundwater quality with respect to Cr(VI) contamination, and (iv) to elucidate the influence of monsoon rain on Cr(VI) mobilization from COPR sites (*Chapter 7*). Therefore, groundwater samples (n = 57 pre-monsoon, n = 70 monsoon) were taken and analyzed for Cr(VI) and relevant hydrochemical parameters. Finally, in *Chapter 8*, the most important results of the study are summarized and their implications for the wider context of waste management strategies for the densely populated region of Kanpur and other Cr(VI) affected areas are discussed.

Chapter 2 Study site

Geographical setting of Kanpur

The study area comprises the region around Kanpur which is located in the state of Uttar Pradesh in North India (Fig. 2.1). This area is bounded by the Ganges in the northeast and by the Yamuna in the southwest. Kanpur is one of the most important industrial centers in northern India and very densely populated.

Fig. 2.1 Geographical setting of the study area.

The study area is part of the central alluvial Ganga plain that was formed in response to the development of the Himalaya (Rao, 1973; Singh, 1996). The major parts of the area are an almost flat plain with some undulations and a slope running from northwest to southeast (Singh et al., 2006). Furthermore, the alluvium is predominantly consisted of Quaternary and recent deposits comprising clay, silt, sand of various grades and gravel.

Climate of Kanpur

The study area is characterized by a humid subtropical climate with cold (November-February), hot (April-June) and monsoon (July-September) seasons. Heavy rainfall occurs during the monsoon season in the months of July, August and September, in which about 80% of the rainfall takes place (data from the meteorological station Kanpur, India Meteorological Department (IMD), 2015). From 1901 to 2000 the average rainfall was 851 mm (IMD, 2015). May is the hottest month of the year with a mean daily maximum temperature of 41.3 °C and mean daily minimum temperature of 28.5 °C (IMD, 2015). With the onset of the monsoon the day temperature drops down considerably.

Sampling sites

The study was carried out in the villages of Rania, 30 km to the west of Kanpur in the district of Kanpur Dehat, as well as Chhiwali and Godhrauli, 40 and 47 km, respectively, to the south-east of Kanpur in the district of Fatehpur in the State of Uttar Pradesh, North India (Fig. 2.1). In these areas active as well as abandoned COPR dumpsites were identified by the organization Ecofriends.

The sampling of COPR material (*Chapters 3* and *4*) as well as uncontaminated soil material (*Chapter 5*) obtained from Rania and Chhiwali took place in October in 2011. Contaminated soil (*Chapter 6*) was obtained from Godhrauli in September 2014. Groundwater samples (*Chapter 7*) were taken in the pre-monsoon period in April 2014 and at the end of the monsoon period in September 2014.

In Rania (Fig. 2.2) the production of BCS commenced in the late 1980s with the first manufacturing unit. In 1992, four manufacturing units were already operating. Chromite ore processing residue from the production of BCS has been illegally disposed on surrounding fields.

Fig. 2.2 Geographical setting of Rania (Google Earth, 2015).

One heap covers an area of ~1 km^2 and contains ~30,000 Mg of waste (Jaiswal and Braun, 2010).The material is not covered by any material but exposed is to the surface. These BCS works closed in 2005 due to raising environmental protest. However, despite the closure of the BCS works, the Cr pollution problem could not be solved, since on the one hand, the COPR is still present in inappropriate landfills, and on the other hand, the works were not finally closed, but rather shifted to other locations. Due to these changes, the factory owner from Rania established two Cr works in Chhiwali (Fig. 2.3) in 2004, which are still in operation. Chromite ore processing residue is disposed of as mentioned above, but the material is covered by a 30-cm-thick layer of quartz sand to hide the waste. In this area the waste is rather dispersed in the village itself or in the surroundings.

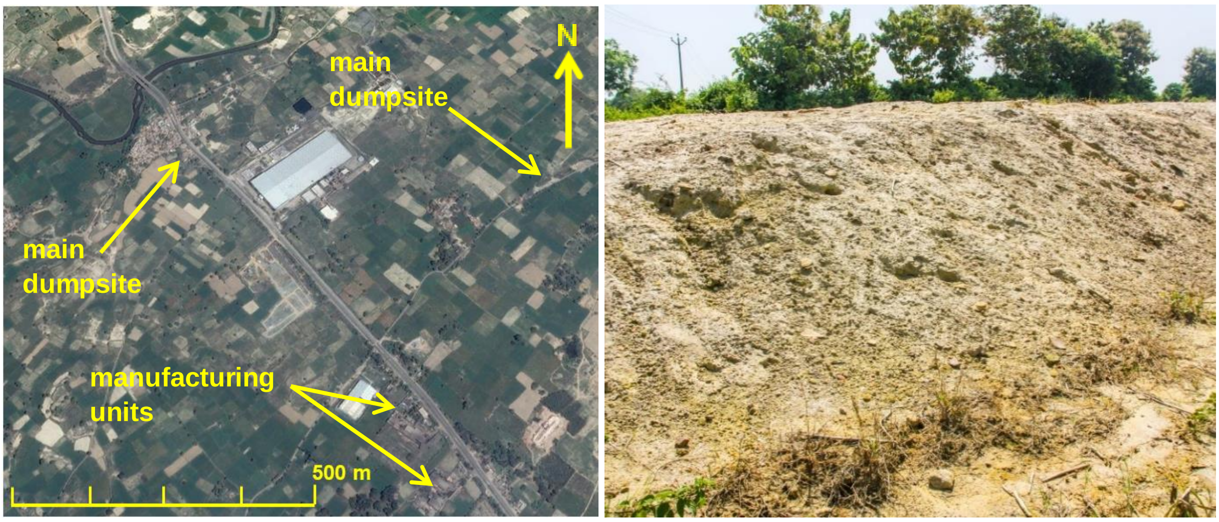


Fig. 2.3 Geographical setting of Chhiwali (Google Earth, 2014a).

In Godhrauli (Fig. 2.4), which is located close to Chhiwali, several illegal waste dumps on an unprecedented scale were installed, although no BCS manufacturing unit is or was present in this village. It can therefore be assumed that the COPR waste derived from the two manufacturing units in Chhiwali.

Fig. 2.4 Geographical setting of Godhrauli (Google Earth, 2014b).

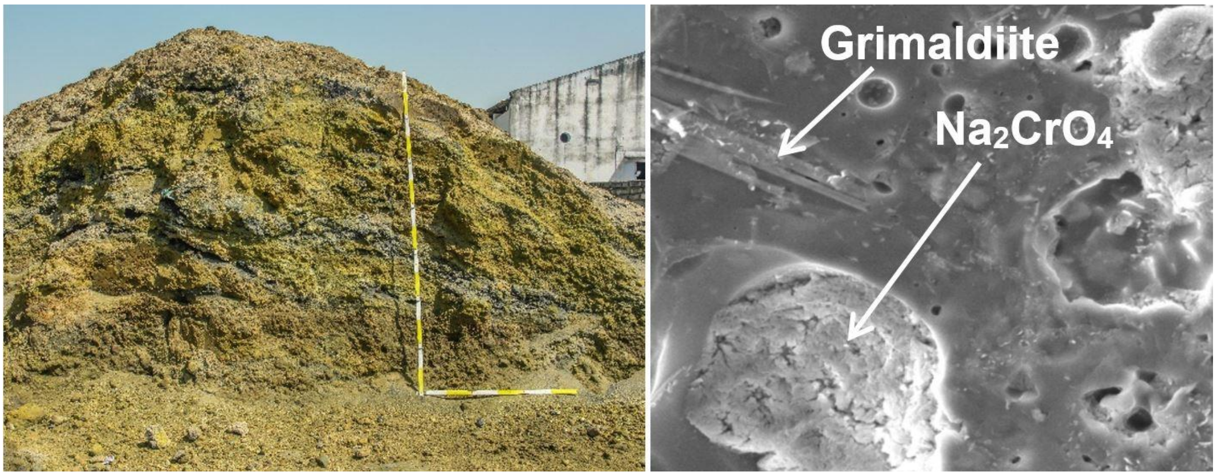
Chapter 3 Chemical and mineralogical characterization of chromite ore processing residue from two recent Indian disposal sites

Chemosphere (2016) 155:188-195

Co-authors: Holger Kletti & Tim Mansfeldt

Formatting and orthography is according to the dissertation style

Graphical abstract



Highlights:

- Relatively young (< 25 years) COPR waste was investigated.
- A new Cr host mineral, grimaldiite [CrO(OH)], could be identified.
- Well soluble Na_2CrO_4 was present in the waste.
- A modified total microwave digestion method was examined.

Abstract

Chromite ore processing residue (COPR) is a hazardous waste. Nevertheless, deposition of COPR in uncontrolled surface landfills is still common practice in some countries. Whereas old (between at least 40 and 180 years) COPR from the temperate zone has been intensively investigated, information on COPR in other regions is restricted. Relatively young (< 25 years) COPR samples obtained from two abandoned landfill sites in India were investigated by a modified total microwave digestion method, X-ray powder diffraction (XRPD), and scanning electron microscopy (SEM) in order to determine their chemical and mineralogical nature. By the use of microwave digestion with acid mixtures of HNO_3, H_3PO_4, and HBF_4 (5:3:2 vol.), COPR was completely dissolved and element contents similar to those obtained by X-ray fluorescence were found. Total Cr contents of the two COPR accounted for 81 and 74 g kg^{-1}, of which 20 and 13% were present in the carcinogenic hexavalent form (CrVI). Apart from the common major mineral phases present in COPR reported earlier, a further Cr host mineral, grimaldiite [CrO(OH)], could be identified by XRPD and SEM. Additionally, well soluble Na_2CrO_4 was present. Improving the effectiveness of chromite ore processing and preventing the migration of Cr(VI) into water bodies are the main challenges when dealing with these COPR.

Keywords

Chromium, Chromite ore processing residue, Speciation, India, Mineralogy

1. Introduction

Chromite ore processing residue (COPR) is a waste of the chromate (CrO_4^{2-}) extraction roasting process and is still deposited in the environment in large amounts in some newly industrialized countries. In the past, the waste has been produced in several industrial areas, such as Glasgow, Scotland (Farmer et al., 1999) and Hudson County, New Jersey, USA (Burke et al., 1991; Weng et al., 1994) and this process is still being used in, for example, China, Russia, Kazakhstan, Pakistan, and India (Darrie, 2001). Darrie (2001) estimated that high-lime process plants generated about 600,000 Mg of COPR in 2001.

Chromite ore processing residue is strongly alkaline, with pH values varying from 11 to 12.5 (Chrysochoou et al., 2009a; Deakin et al., 2001; Foeldi et al., 2013). Residual Cr contents of waste COPR range from 20 to 110 g kg^{-1} (Farmer et al., 1999; Foeldi et al., 2013; Geelhoed et al., 2003), of which up to 30% is present as hexavalent Cr (CrVI) (Geelhoed et al., 2003). After deposition, COPR is not stable and undergoes weathering reactions, which results in destabilization and dissolution of Cr(VI)-bearing minerals (Chrysochoou et al., 2010; Geelhoed et al., 2002; Geelhoed et al., 2001). Hence contamination of groundwater is a key environmental risk arising at COPR sites.

In a previous work (Foeldi et al., 2013), we investigated 21 samples from uncontrolled operating disposal sites and surrounding soils in the area of Kanpur, Uttar Pradesh, North India. These sites were affected by the production of Cr tanning agents. Considering that six samples were clearly identified as highly Cr-contaminated COPR (Foeldi et al., 2013), a detailed study of the mineralogy and chemistry of the source COPR is needed.

This study focuses on two production sites of Cr(III) salts used in leather tanning near Kanpur. The first site reported in this paper is Rania, to the west of Kanpur in the district of Kanpur Dehat, where Cr works were in operation from the late 1980s until 2005. One heap covers an area of ~1 km^2 and contains ~30,000 Mg of waste (Jaiswal and Braun, 2010). At the second site, in Chhiwali, to the southeast of Kanpur in the district of Fatehpur, two Cr works were established in 2004 and are still operating. Chromite ore processing residue is found in large landfill sites as well as elsewhere in these areas, because it is commonly used in road construction, berms, and foundation material and for backfill, due to its sand-like properties.

Although the mineralogy and solid-state speciation of Cr in COPR deposits have been widely studied in the USA (Boecher et al., 2012; Chrysochoou and Dermatas, 2007; Chrysochoou et al., 2009a, 2010; Dermatas et al., 2006) and Europe (Farmer et al., 1999; Geelhoed et al., 2002; Hillier et al., 2003; Thomas et al., 2001), the present findings cannot be simply transferred to the Indian sites: COPR from various localities may differ in their chemical and mineralogical compositions due to differences in (i) chromite ore composition, (ii) extraction process, (iii) deposition technique, and (iv) ambient weathering conditions. Previous studies have investigated COPR from sites located in the temperate zone. The Indian sites, however, are in the humid subtropical climate zone with a dry winter season and a three-month monsoon period. Finally, (v) the factor of time is different because the Indian COPR are relatively young (< 25 years) compared to the Glasgow and North American COPR (between at least 40 and 180 years).

Thus, the aim of the present study was to investigate the chemical and mineralogical characteristics of COPR obtained from two abandoned landfill sites in India. We expected that the Cr content of these COPR would be higher compared to the Glasgow and North American COPR, because of the limited leaching time during the monsoon period as well as the short time of landfilling. We also assumed that the mineral phases would differ, which might be important regarding the leaching behavior of these COPR. Scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD) complemented by other laboratory analyses were performed to investigate these objectives. Furthermore, a modified total microwave digestion method was examined, since it is important to evaluate different methods to accurately determine the total Cr contents of the waste. The results presented in this study provide an improved understanding of these COPR wastes and are essential for the evaluation of environmental risks and remediation strategies.

2. Material and methods

2.1 Sites, sampling, and sample preparation

The COPR was sampled from two abandoned, illegally operating disposal sites in Rania and Chhiwali in the State of Uttar Pradesh. In Rania, surface COPR was taken with a spade from a 20-year-old landfill, which was not covered by any material but left exposed to the surface. In Chhiwali, COPR was obtained at the edge of a 10-year-old landfill which had a thickness of about 6 m and was covered by a 30-cm-thick layer of quartz sand. Sampling took place during the dry season in order to obtain dry material. The samples were manually homogenized by intensive stirring for 10–15 minutes with a big shovel, air dried, and sieved (< 2 mm). Particles > 2 mm were separated for backscattered electron (BSE) images and secondary electron (SE) images. Subsamples were ground in an agate ball mill (PM 400, Retsch).

2.2 Analyses of chemical composition

Particle size distribution was analyzed with a laser particle analyzer (Beckman Coulter LS13 320). Prior to the analyses, carbonates were destroyed with HCl. The COPR pH was measured potentiometrically using a glass electrode (Unitrode, Metrohm) both in 0.01 M $CaCl_2$ solution and in deionized water with a solid:solution ratio of 1:5. Total C, N, and S were quantified with a CNS analyzer (Vario EL, Elementar). 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. The chemical composition was analyzed by wavelength dispersive X-ray fluorescence (XRF; Axios, PANalytical, further details are provided in supplementary materials (SM)).

Due to the importance of accurate determination of the total Cr content of the waste, two different total digestion methods were evaluated. Since it is used by researchers in many countries for the determination of metals, a pseudo-total aqua regia digestion method was also performed. Detailed information on the digestion methods are listed in the SM.

Chromate in the wastes was selectively extracted with (1) deionized water (pH 5.7) for soluble CrO_4^{2-}, (2) phosphate buffer (5.0 mM K_2HPO_4 in 5.0 mM KH_2PO_4, pH 7.0) for exchangeable CrO_4^{2-}, and (3) carbonate-hydroxide solution (0.28 M Na_2CO_3 in 0.5 M NaOH, pH 11.8 to12.3) for insoluble CrO_4^{2-} according to James et al. (1995) (further details are provided in the SM). Since in a previous study by Farmer et al. (2006) it was found that milling the COPR prior to base digestion almost doubles the release of Cr(VI), additionally milled samples were used in step 3. Chromium(VI) concentration in the eluates was determined spectrophotometrically at 550 nm (Lambda 25 UV/Vis Spectrometer, PerkinElmer) with diphenylcarbazide (US EPA, 1992) immediately after filtration.

2.3 Analyses of mineralogical composition

The X-ray diffraction measurements were recorded on a Bruker D8 Advance diffractometer in Bragg-Brentano geometry. The wavelength used was Cu Kα radiation generated at 40 kV and 40 mA and selected via a Bruker SolX energy dispersive detector. The measurement range was 4° 2θ to 70° 2θ with a step size of 0.02° and a counting time of 4 s per step. Each sample was measured twice. Sample preparation and phase identification are described in the SM.

For SEM, all samples were examined in an FEI Nova NanoSEM 230, an ultra-high resolution SEM with low vacuum, using a beam accelerating voltage of 12 kV. Quantitative and qualitative elemental analyses were performed with an energy-dispersive X-ray (EDX) spectrometer fitted with a 40 mm^2 silicon drift detector (Apollo 40 Edax/Ametek). For imaging of the morphology and texture of fractured sample surfaces, an SE signal was used. Detailed information on sample preparation and interpretation are provided in the SM.

3. Results and discussion

3.1 Analyses of the chemical composition

Table 1 summarizes the physical and chemical properties of the COPR. The particle-size distributions of the two COPR were similar. Three-quarters of the material had a particle size between 2 and 0.2 mm. The rest of the material was silty with small amounts of clayey particles. Dermatas et al. (2006) also investigated the particle size distribution of some COPR and classified them as silty sands. Differences in particle size distribution result from mineralogical differences, storage of such waste, and stage of weathering, or the deaggregation of COPR grain agglomerations produced by the preparation method. It is often observed that many particles are cemented together and form larger agglomerations of COPR (Dermatas et al., 2006; Hillier et al., 2003). Exposed COPR also forms crusts due to weathering processes.

Both COPR had highly alkaline pH of 12.4, which is around the pH of saturated lime water (12.4) (Hausmann, 1990), due to the use of lime (CaO) during the roasting process. This alkaline pH regime favors the stability and mobility of hexavalent Cr as the oxyanion CrO_4^{2-}.

Table 1 Physical and chemical properties of the COPR.

		Rania	Chhiwali
Sand (2–0.2 mm)	(g kg^{-1})	790	720
Silt (0.2–0.002 mm)	(g kg^{-1})	190	240
Clay (< 0.002 mm)	(g kg^{-1})	20	40
pH in H_2O	(–)	12.4	12.4
pH in $CaCl_2$	(–)	12.4	12.4
Total C	(g kg^{-1})	20.7	14.8
Inorganic C	(g kg^{-1})	18.7	13.1
Organic C	(g kg^{-1})	2.0	1.7
Total N	(g kg^{-1})	0.4	0.3
Total S	(g kg^{-1})	0.3	0.4
Al	(g kg^{-1})	44.3	48.8
Ca	(g kg^{-1})	225	227
Cr	(g kg^{-1})	79.8	75.5
Cu	(g kg^{-1})	0.04	0.05
Fe	(g kg^{-1})	73.2	83.8
K	(g kg^{-1})	0.67	1.00
Mg	(g kg^{-1})	47.3	60.4
Mn	(g kg^{-1})	1.29	1.21
Na	(g kg^{-1})	4.37	6.80
Ni	(g kg^{-1})	0.79	1.21
Si	(g kg^{-1})	39.0	49.1
O	(g kg^{-1})	278	306
LOI[a]	(g kg^{-1})	200	132

[a] Loss on ignition

The total C content were 14.8 (Chhiwali) and 20.7 g kg^{-1} (Rania), of which approximately 90% was present as inorganic carbon. The total N and S contents were 0.3 and 0.4 g kg^{-1} and therefore similar for both COPR samples. The main elements in the COPR were Al, Ca, Cr, Fe, Mg, and Si. Sodium and K occurred only in lower contents. The Al, Ca, Mg, K, and Na contents of the Indian COPR are in the range of the COPR obtained from the US and Glasgow. The Si content is distinctly higher (4–10-fold) and the Fe content is 0.25- to 2-fold lower than in US COPR (Boecher et al., 2012; Chrysochoou et al., 2010), whereas these two elements do not differ from Glasgow COPR values (Hillier et al., 2003). Differences in these element contents may arise from the variation in the composition of the original ore. It can be assumed that the ore used in the roasting process in India and Glasgow was magnesiochromite ($MgCr_2O_4$), due to the lower Fe and higher Mg contents (Hillier et al., 2003). However, the different Si content may arise from impurities of Si in the ore or admixtures of non-COPR material like sand or soil.

The total metal contents in different materials have been investigated by a variety of digestion techniques, for example microwave-assisted according to US EPA 3052 (US EPA, 1996) and pressure bomb (Sun et al., 2001), and these methods have several additional alternative acid and reagent combinations. Since the chromite ore is known to be acid resistant, only a few methods are useful for accurately determining the total element contents in COPR. Hence two modified total digestion techniques were evaluated. Both the pressure bomb digestion and the microwave digestion were able to totally dissolve the two COPR samples. Nevertheless the reference materials CHR-Bkg and CHR-Pt+ (both GIT-IWG, Geostandards, France) could not be dissolved by the pressure bomb technique, despite the use of HF. For the COPR samples and the reference material SARM 8 (Mintex, South Africa), the element contents obtained by the pressure bomb digestion equaled those obtained by XRF (Table 2, SM Table S2).

Table 2 Comparison of total chromium contents (g kg^{-1}) of two Indian COPR samples (Rania and Chhiwali) and three certified reference materials determined by microwave digestion, pressure bomb digestion, and X-ray fluorescence (XRF).

	Rania	Chhiwali	SARM 8[a]	CHR-Bkg[b]	CHR-Pt+ [c]
Microwave digestion	81.2	73.5	321	190	144
Pressure bomb digestion	80.6	71.9	321	153	123
XRF	79.8	75.5	—[d]	—	—

[a] 335 g kg^{-1}

[b] 199 g kg^{-1}

[c] 139 g kg^{-1}

[d] Not determined

Only Si could not be measured after digestion, because Si degassed during the vaporization step due to the formation of tetrafluorosilane (SiF_4). The lack of success of pressure bomb technique for the reference materials CHR-Bkg and CHR-Pt+ was revealed by the underestimation of Cr by –23 and –12%. Weng et al. (1994) also reported that the use of the acid mixture HNO_3/HCl or HCl/HF leads to the underestimation of element contents. Morrison et al. (2009) determined that a 4-acid digestion (HNO_3, HCl, HF, $HClO_4$) only partially dissolves chromite. However, the use of HF already significantly increased metal extraction, especially for Cr, Fe, and Mg, which were the main elements of the chromite ore. With the microwave digestion technique, both samples and all reference materials were totally dissolved and the element contents corresponded to those of the XRF analyses and the certified reference values (Table 2, SM Table S2). Apparently the additional use of H_3PO_4 and the high temperature enhanced the digestion. A further advantage of the use of HBF_4 instead of HF is the simplified handling without loss of analytical quality. Therefore the microwave digestion with use of concentrated HNO_3, H_3PO_4 and HBF_4 (see also SM) might be a suitable method for total element analyses in COPR.

As mentioned above, the widely used aqua regia microwave digestion using the acid mixture of HNO_3 and HCl resulted in significantly lower Cr contents than XRF. Only 42 and 39% of the total Cr could be recovered for the Rania and Chhiwali samples, respectively (Table 3). Therefore it can be assumed that chromite cannot be totally dissolved by aqua regia microwave digestion. The measured Cr was obtained from other Cr-hosting mineral phases or partially from chromite since acid digestion can etch chromite, even if it does not completely dissolve it (Morrison et al., 2009).

Considering that between 80 and 87% of the Cr was present as Cr(III), from which most was present as unreacted ore, it can be concluded that the roasting process used in the Kanpur region is inefficient. Assuming that there was 33–39% Cr in the original ore (data not published), the extraction efficiency was around 75–80%. The efficiency of chromate extraction is strongly dependent on the mineral composition of the ore since its composition and mineralogical characteristics influence the kinetics of the roasting process (Tathavadkar et al., 2001). However the extraction efficiency is higher than reported by Tathavadkar et al. (2001), who stated an efficiency below 45 % for Indian ore.

The results of the Cr(VI) extraction are presented in Table 3. With the carbonate hydroxide solution at 85 °C, 16.5 and 9.2 g kg^{-1} Cr(VI) were extracted from the Rania and Chhiwali samples, respectively, but it could not be confirmed that milling the COPR prior to base digestion almost doubles the release of Cr(VI) (Farmer et al., 2006). An increased Cr(VI) content of 1.8 g kg^{-1}, which amounts to 25%, could be measured only for the Chhiwali sample. Hence encapsulation of Cr(VI) compounds by other compounds/minerals does not seem to be as important.

Table 3 Chromium contents (g kg^{-1}) extracted by a mixture of $HNO_3/H_3PO_4/HBF_4$ and aqua regia as well as Cr(VI) contents extracted by carbonate-hydroxide (CH)/85 °C, phosphate buffer (Pbuff), and deionized water.

	Rania		Chhiwali	
Total Cr (Microwave)	81.2	(100%)	73.5	(100%)
Cr aqua regia	33.7	(42%)	28.9	(39%)
Cr(VI) CH	16.2	(20%)	7.4	(10%)
Cr(VI) CH fine	16.5	(20%)	9.2	(13%)
Cr(VI) Pbuff	1.85	(2.3%)	1.05	(1.4%)
Cr(VI) water	1.38	(1.7%)	0.75	(1.0%)

The other three extraction methods only dissolved small amounts of Cr(VI) ranging from 1.4−1.9 g kg^{-1} for Rania and 0.75–1.05 g kg^{-1} for Chhiwali samples. Altogether, 20% (Rania) and 13% (Chhiwali) of the total Cr were present as hexavalent Cr in insoluble Cr(VI)-bearing mineral phases and only 1–2.3% was in easily soluble or exchangeable form (Table 3). The high content of total Cr and the low percentage content of Cr(VI), especially for the Chhiwali sample compared to COPR from the US (Chrysochoou et al., 2009a) and Glasgow (Farmer et al., 2006; Geelhoed et al., 2003), may arise from the low age and thus the shorter weathering time of these COPR. It is probable that under ambient long-term conditions, residual Cr(VI) is only stepwise leached during the short monsoon period with annually precipitation of about 800 mm, if the binding capacity of the material for Cr(VI) has been exhausted. The COPR obtained from US and Glasgow was subject to higher annual precipitation (> 1100 mm) without dry season. Furthermore, the high Cr content may also be a result of the inefficiency of the roasting process. The extraction of Cr from chromite ore is dependent on roasting temperature and time (Tathavadkar et al., 2001), however, the Cr works in this area do or did not have any temperature control. Considering that the Cr content of the original ore was around 330–390 g kg^{-1} (unpublished data), the extraction rate is around 80%. It should be noted that the soda-ash roasting process is inefficient in general, which is reflected in maximum extraction rates of 80–90% (Antony et al., 2006).

3.2 Analyses of mineralogical composition

Figure 1 shows the XRPD patterns of both COPR, in which a total of 13 crystalline phases were identified. Indicative structural formulae are listed in Table S1 of the supplementary material. According to Hillier et al. (2003), minerals and compounds identified in COPR can be divided into three groups: i) unreacted feedstock ore, ii) "parent" minerals produced during the high-temperature roasting process, and iii) minerals formed during the final stage of leaching to recover the soluble Cr salts or formed under ambient weathering conditions at the disposal sites. The qualitative analyses of the two COPR patterns showed the same phase assemblages with few minor differences, although their composition was very complex (Fig. 1).

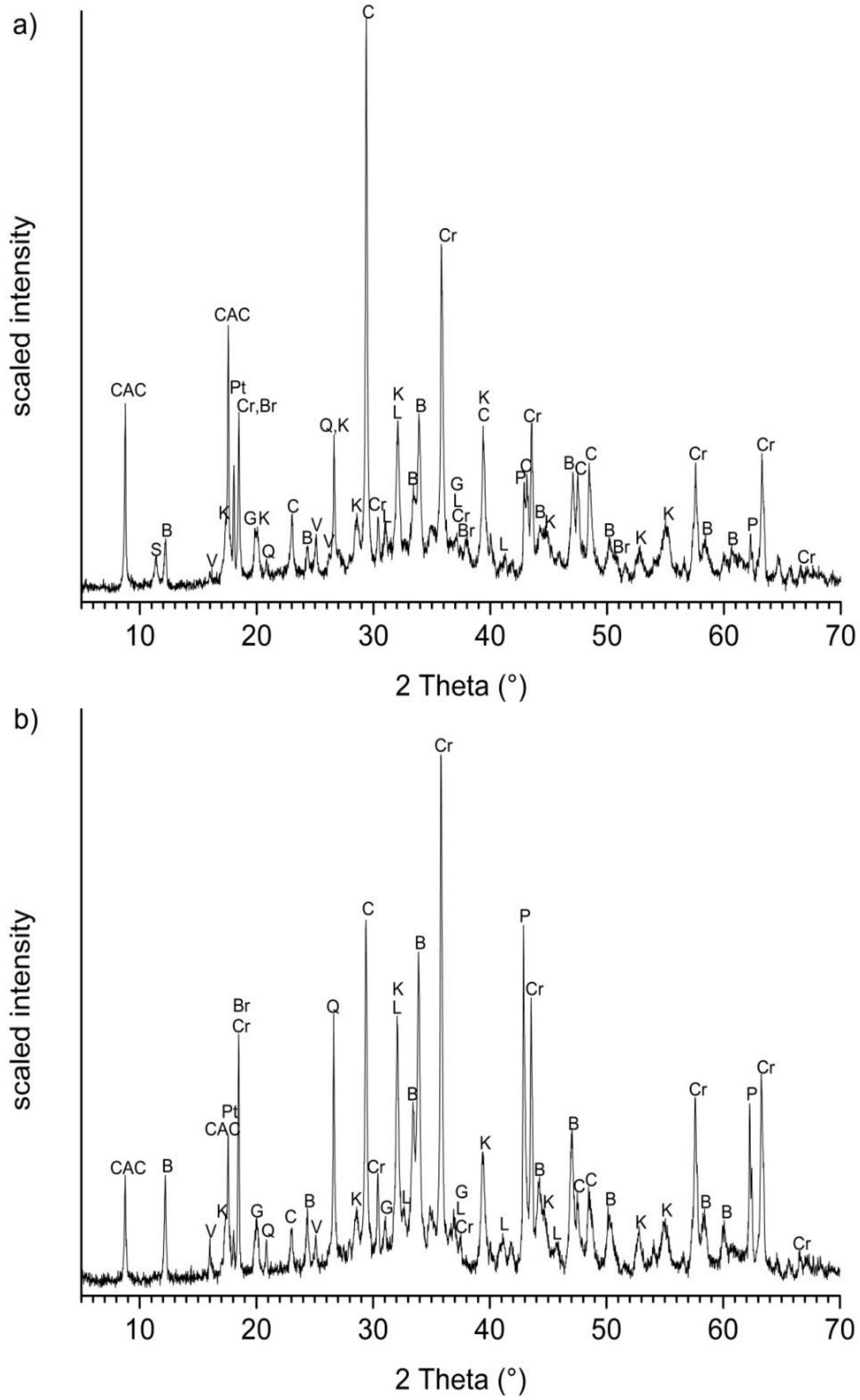


Fig. 1 Powder X-ray diffraction patterns of COPR from (a) Rania and (b) Chhiwali. The identification of the main reflexes is indicated and the patterns are offset for clarity. B: brownmillerite; Br: brucite; C: calcite; CAC: calcium aluminum chromium oxide hydrate; Cr: magnesiochromite; G: grimaldiite; K: katoite; L: larnite; P: periclase; Pt: portlandite; Q: quartz; S: sjogrenite; V: voltaite.

The first group includes only one mineral, the chromite, which was identified in both COPR by the dominant reflexes at ≈18.42°, ≈36.04°, ≈43.40°, ≈57.86°, and ≈63.39° 2θ. Due to the reflexes and the relatively high Mg content obtained from EDX analyses, magnesiochromite might be the dominant ore used in the roasting process. Furthermore chromite could be easily recognized in BSE images of the COPR (Fig. 2a, b, Fig. S1a, b).

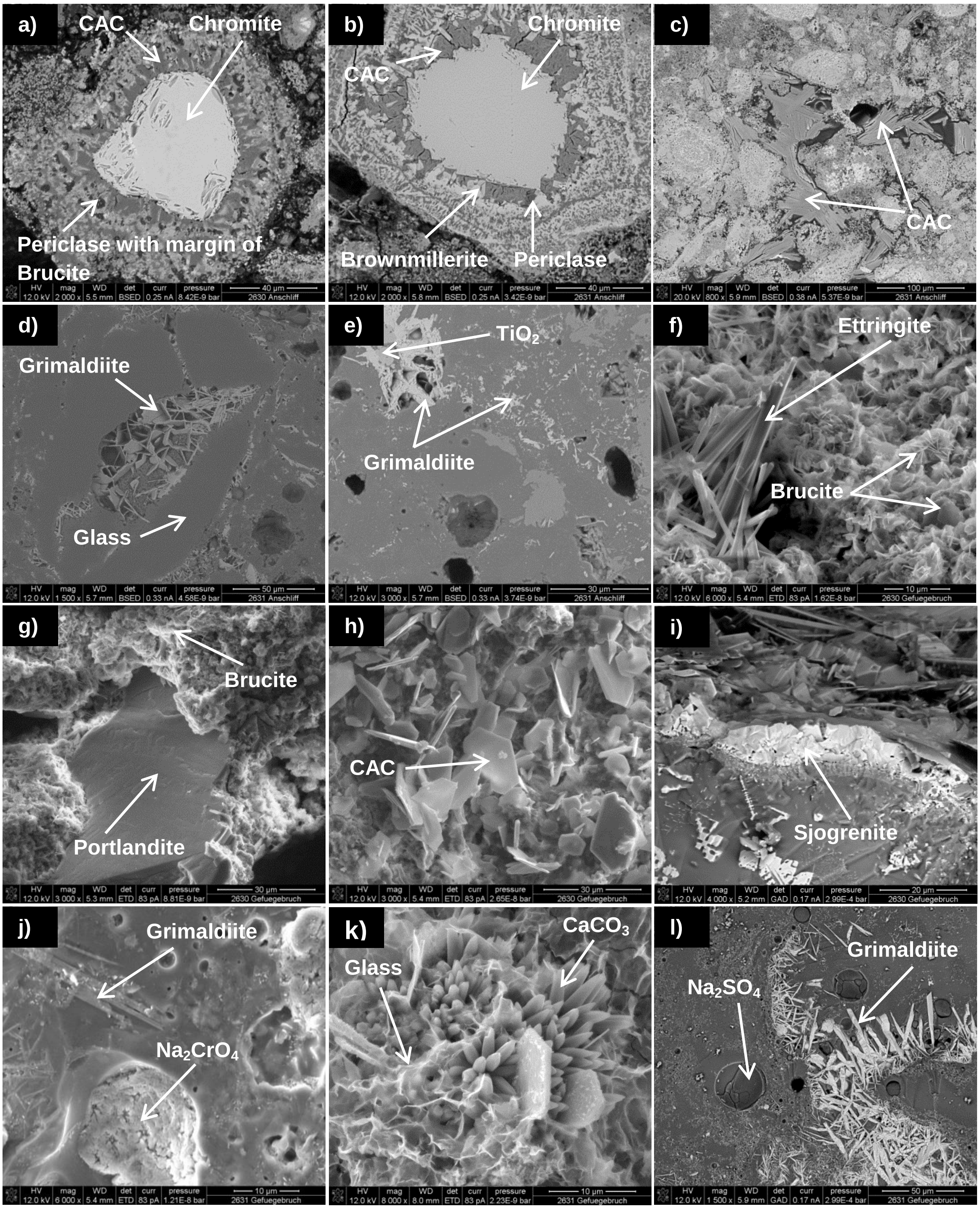


Fig. 2 Backscattered electron images (polished surfaces a, b, c, d, e) and secondary electron images (fractured surfaces f, g, h, I, j, k, l) of solid phases in COPR. Samples originated from Rania (a, f, g, h, i) and from Chhiwali (b, c, d, e, j, k, l).

The chromite grains were surrounded by concentric zones of other phases with the appearance of an alteration halo, as previously reported by Hillier et al. (2003). Because chromite is known to be extremely resistant to weathering (Kostov, 1968), such halos consist of phases produced during the high-temperature treatment of the ore and following alteration by weathering. The type of ore and the content of gangue minerals, such as silicates, is important for the success of the roasting process (Antony et al., 2001) and thus, for the remaining Cr(III) in the COPR. Furthermore, its composition determine its suitability for the use in alternative free-lime roasting processes that would overcome the formation of highly toxic $CaCrO_4$ and reduce alkalinity, thus facilitating the treatment of COPR.

Phases typical for the second group are brownmillerite, larnite, periclase, and portlandite and were identified by XRPD (Fig. 1). Brownmillerite was detected by a multiplicity of reflexes at ≈12.3°, ≈32.17°, ≈33.80° and ≈47.09° 2θ. Regarding the relative intensities of reflexes, the sample from Chhiwali apparently had a higher brownmillerite content than the Rania sample. In BSE images (Fig. 2b, Fig. S1b), it is very obvious that brownmillerite occurred as a part of a rim or halo around other phases, for example around chromite, whereas in the Rania sample it was disseminated throughout the COPR (Fig. S1a). Regarding its composition, most grains were rich in Fe and Al, but there was also substitution of Cr. However, it is not clear whether or not brownmillerite undergoes hydration after deposition. Wazne et al. (2008) stated that brownmillerite hydration is kinetically inhibited in the COPR material, especially if Mg constitutes approximately 6% of the COPR. In contrast, Chrysochoou et al. (2010) reported that brownmillerite is unstable in ambient temperature and aqueous environments and hydrate to form katoite. Nevertheless, brownmillerite seems to be stable over a long period, which may explain its persistence in older COPR material obtained from Glasgow and the USA.

Larnite, a further mineral of the high-temperature phases, was identified by two small reflexes at ≈31.08°, and ≈41.19° 2θ in the XRPD patterns. The identification of larnite by SEM was unsuccessful; however Si was often found in a fine-grained matrix associated with Al, O, and Ca, which can be assigned to feldspar (a non-COPR compound). Larnite was also identified in COPR obtained from Glasgow (Hillier et al., 2003), however its presence in COPR from the USA was not described.

Periclase was identified by two reflexes at ≈42.91° and ≈62.30° 2θ in the XRPD patterns as well as in BSE images (Fig. 2a, b), where it was an abundant component in both samples. It is noticeable that in the Chhiwali sample higher contents of periclase, which was not rimmed by other phases, occurred, whereas the Rania sample had lower contents and the mineral was rimmed by its hydration product, brucite. That may arise from the fact that the Rania sample is older and thus more strongly weathered. Periclase was also detected in older COPR obtained from Glasgow and the USA. Hillier et al. (2003) reported that periclase is rimmed by other phases in the Glasgow COPR and thus protected from hydration to brucite in the interior of nodular masses, which may account for its persistence in older COPR. Portlandite may also be considered as a COPR parent mineral as it formed rapidly upon hydration of excess quicklime during the early stages of transport and deposition (Chrysochoou et al., 2010) and was identified by a reflex at ≈18.09° 2θ as well as by an SE image of fractured surfaces (Fig. 2g).

The third group includes the minerals aragonite, brucite, calcite, calcium aluminum chromium oxide hydrate (CAC), ettringite, katoite, and sjogrenite. Brucite develops by hydration from the unstable periclase during weathering and was detected in both COPR by BSE (Fig. 2a, Fig. S1a) and SE (Fig. 2f, g) images. It is obvious from the BSE images that the Rania sample was more weathered compared to the Chhiwali sample, because the periclase was entirely transformed to brucite or distinctly rimmed by brucite, whereas in the Chhiwali sample the periclase was marginally associated with brucite. This is also confirmed by the XRD patterns, in which brucite was just detectable by only one reflex at ≈18.59° 2θ for the Chhiwali sample and two more reflexes at ≈38.02° and ≈50.85° 2θ for the Rania sample, as well as the higher relative intensity for periclase in the Chhiwali sample. Whether or not brucite and portlandite can bind Cr(VI) is controversial, but Ginder-Vogel et al. (2005) found that Cr(VI) was bound to portlandite ($Ca(OH)_2$) grains, although they did not clarify the binding mechanism. From the EDX analyses of the COPR used in this study it can be assumed that Cr(VI) binding on the abovementioned minerals is not relevant. Even if Cr(VI) would be present in brucite, the mineral should remain stable in the COPR at pH values above 12, where the pH is too high for dissolution.

The calcium carbonate present in the samples (Table 1) can be attributed to calcite, because in XRPD patterns calcite was clearly identified by the reflexes at ≈13.04° and ≈29.40° 2θ. An SE image (Fig. 2k) also showed the presence of calcium carbonate in an acicular form with chisel-like terminations, which is characteristic for aragonite (Hillier et al., 2003), which could not be detected by XRPD. In further SE images (data not shown), calcium carbonate also occurred in a blocky form or coated with a gel matrix, and the former form may also be identified as calcite (Hillier et al., 2003). The formation of carbonate phases occurs directly from any Ca source when CO_2 is sequestered into solution due to the strongly alkaline pH (Chrysochoou et al., 2010).

CAC, also known as Cr(VI)-hydrocalumite, was identified in both COPR by a strong reflex in the XRPD patterns at ≈8.71° 2θ and by the abundant occurrence of hexagonal crystals with a plate-like morphology in SE images (Fig. 2c, h). It is a layered double hydroxide mineral known to have a high anion exchange capacity with CrO_4^{2-} anions held in the interlayers (Palmer, 2000; Wazne et al., 2008). The CACs are a group of minerals which have similar structures with varying degrees of hydration (Chrysochoou and Dermatas, 2007). Due to the reflex in XRPD patterns it can be assumed that CAC-14 was the predominant form in the two samples. Based on BSE images and EDX analyses (Fig. S1a, b) two different types of CACs could be distinguished: One type consisted of large amounts of Al and Cr; it rimmed the magnesiochromite ore or was distributed in the periphery. The other type was more Fe-rich but contained lower Cr contents and was located at some distance from the magnesiochromite core. Since CAC is a hydration product of brownmillerite, the development of several intermediate products during the hydration process is likely. Calcium aluminum chromium oxide hydrate was also reported in COPR materials obtained from Glasgow (Hillier et al., 2003) and the USA (Chrysochoou and Dermatas, 2007).

Ettringite is another brownmillerite hydration product and is the most stable of the hydration products in the presence of sulfate. Secondary electron images were the only evidence for the presence of ettringite in the Rania sample, where it was notable due to its needle-like long prismatic habit (Fig. 2f). Many researchers have shown that CrO_4^{2-} may substitute for SO_4^{2-} in ettringite. Hillier et al. (2007) observed up to 50% CrO_4^{2-} substitution in ettringite crystals in Glasgow COPR. In the Rania sample, EDX analysis also indicated the existence of CrO_4^{2-} rich species. However, Chrysochoou and Dermatas (2007) reported the presence of ettringite in COPR materials obtained from the USA as pure sulfate species with negligible CrO_4^{2-} substitution.

Katoite, often denoted as hydrogarnet, is a Ca aluminate which develops by hydration of brownmillerite. The XRPD pattern of katoite was very distinctive, with reflexes at ≈17.35°, ≈19.98°, ≈39.32°, ≈52.29°, and ≈54.73° 2θ, whereas several reflexes show overlaps with other mineral phases. It is obviously a major component of the COPR not only in the Indian COPR, but also in COPR material obtained from Glasgow (Hillier et al., 2003) and the USA (Chrysochoou and Dermatas, 2007), which is important regarding the substitution of Cr(VI) in the tetrahedral structure (Hillier et al., 2007; Hillier et al., 2003).

Sjogrenite, often named as hydrotalcite, can be formed from periclase or brucite when sufficient Al is released from brownmillerite hydration (Wazne et al., 2008). In the Rania COPR it was identified by a reflex at ≈11.35° 2θ and by an SE image in which a cluster of sjogrenite crystals was obvious (Fig. 2i). EDX spectrometer analyses indicated the substitution of Cr in the mineral structure. Sjogrenite has a similar structure to CAC and also belongs to the general group of layered double hydroxides with differences in the chemical composition (CAC consists of Ca, Al, and CrO_4^{2-}, while sjogrenite consists of Mg–Fe carbonate compounds). It is possible that sjogrenite also retains CrO_4^{2-} in the interlayer, apart from carbonate and/or hydroxyl (Chrysochoou and Dermatas, 2007).

Furthermore, two mineral phases were present in the Indian COPR which were not previously detected in COPR by other researchers. The first one is grimaldiite, a chromium oxide-hydroxide [CrO(OH)]. The presence of grimaldiite was identified in both COPR by a strong reflex at ≈19.98° 2θ in the XRD patterns. The identification was not easy, because the main reflex was close to those of katoite at ≈20.09° 2θ. Additionally, the second reflex was also shared with other mineral phases such as larnite and magnesiochromite at around ≈37.33° 2θ. However, grimaldiite was also identified in the Chhiwali COPR by EDX (Fig. S2), BSE (Fig. 2d, e), and SE images (Fig. 2j, l) with a needle-like habit. Considering that grimaldiite was not identified in the Rania sample by BSE and SE images, the reflex of the XRD pattern can only be taken as an indication of the presence of grimaldiite in this COPR. Natural occurrences of the rhombohedral CrO(OH) are in fine-grained intergrowth with other chromium oxide-hydroxide minerals in alluvial gravels in the basin of the Merume River, Guyana (Milton et al., 1976) and in cracks and crevices in penroseite from a hydrothermal mineral deposit in the Hiaca mine in Bolivia (Livingstone et al., 1984).

The second mineral is voltaite, which was identified by two reflexes at ≈15.90° and ≈25.14° 2θ in XRPD. Furthermore it is probable that it only occurs in low contents, because of the relatively low reflex intensity. Although K occurred in COPR (Table 1), no K-containing mineral phase has yet been described, which could also be evidence for the presence of voltaite. Voltaite was originally described as a mineral from fumaroles and solfataras in the volcanic field of southern Italy (Majzlan et al., 2013), but it is also an alteration product in mineral deposits high in pyrite, especially in arid climates, where it is also a post-mining product. Furthermore Giere et al. (2007) reported the emission of voltaite from a coal-fired power plant. Since voltaite is not associated with chromite (personal communication, Majzlan, J.), it originates rather from the high-temperature roasting process. So far, the origin of these two mineral phases in the Indian COPR has not been clarified and therefore further investigations are required.

Another special feature is the existence of easily soluble compounds, such as Na_2CrO_4 and Na_2SO_4, which have not previously been found in COPR. They were present in pores in the Chhiwali COPR (Fig. 2j, l) and therefore were possibly protected from leaching. However in the European and North-American COPR, only the moderately soluble phase chromatite ($CaCrO_4$) was described in some samples (Chrysochoou et al., 2009b; Geelhoed et al., 2002). Sodium chromate probably remained from the leaching step during the production process. Otherwise, James (1994) reported that crusts containing CrO_4^{2-} salts have appeared on the surface of poorly drained soils, due to evaporation of soil water containing soluble CrO_4^{2-}. The crust formation appears during dry periods when evaporation of water occurs on the surface, and is not visible when rainwater dissolves the salts again (James, 1994). This might also be applicable for the Indian COPR due to the short monsoon period and the longer-lasting dry season. The absence of easily soluble phases in the COPR materials obtained from Glasgow and the USA may be attributed to the higher age of these materials and the prevailing weathering conditions (e.g. higher annual precipitation), as it is likely that the easily soluble phases were already leached out.

Apart from mineral phases of the COPR-related process, the samples also contain non-COPR compounds such as quartz and TiO_2. Quartz is derived from the sand covering of the COPR

(Chhiwali) or from native soil (Rania) and was detected in both samples by two reflexes at ≈20.85° and ≈26.65° 2θ. The fact that in Chhiwali the COPR was covered by a sand layer is reflected by the higher quartz reflex in this sample as well as the higher Si content determined by XRF. The presence of soil material is potentially important for COPR as a soluble silica source, especially at high pH, for cementitious reactions that form crystalline afwillite and x-ray amorphous calcium silicate hydrates (Dermatas et al., 2006), which certainly could not be detected in the COPR used for this study.

3.3 Environmental significance

The differences in chemical and mineralogical properties between the COPR materials have important implication for its leaching behavior and thus for the treatment of these materials. As described for the COPR material in Glasgow and the USA, Cr(VI) in the Indian COPR is predominantly bound in minerals such as CAC, ettringite, katoite, and sjogrenite. However, as long as the pH in the COPR does not decreased below 12, the release of Cr(VI) will be slow. A main problem is that the Indian COPR also contained easily soluble compounds, such as Na_2CrO_4 that are leached even at pH values higher than 12. In addition to it, Cr(VI) is partially present in pores, which makes treatment of the COPR difficult, because much of the Cr(VI) seems to be not accessible to reductants such as $Fe(II)SO_4$ or CaS_5. In this case, the addition of a stepwise reductant is required and a long curing time is necessary. Farmer et al. (2006) reported that capping of COPR dumpsites is recommended at least as a short- to medium-term measure, which is already in practice at most of the COPR-impacted sites in the Glasgow area. This could also be a measure for the Indian sites to minimizes the potential for Cr(VI) leaching. However, leaching behavior of the investigated Indian COPR must be investigated at first, since the direct transfer of leaching behavior from one matrix to another is very limited due to the complexity of COPR.

4. Conclusion

Our results show that COPR originating from Rania and Chhiwali differ from European and North-American COPR. First of all, the chromite ore used in the Indian roasting process was magnesiochromite instead of ferrochromite used in New Jersey. Secondly, the CrO_4^{2-} extraction process was very inefficient, which is reflected in the high Cr content. Both the roasting of the ore as well as the leaching process need to be improved in order to protect the environment and to conserve resources. Due to the high remaining Cr content, remediation is needed, or another approach worth considering is mining of the waste. Thirdly the open deposition of the waste and the long-lasting dry season led to the presence of highly soluble CrO_4^{2-} phases, resulting in the contamination of groundwater bodies that is already observed in some wells. Fourthly, the age of the COPR was crucial to its mineral composition, especially with regard to the weathering of the high-temperature mineral phases and their transformation. Finally, grimaldiite and voltaite were detected in COPR for the first time. In addition, the modified microwave digestion was an appropriate method for the determination of total metal contents in COPR.

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Supplementary material

Chemical and mineralogical characterization of chromite ore processing residue from two recent Indian disposal sites

1. Descriptions of methods

X-ray fluorescence spectroscopy (XRF)

Powdered samples were mixed with a flux material and melted into glass beads. To determine the loss on ignition, 1000 mg of sample material was heated to 1030 °C for 10 minutes. After mixing the residue with 5.0 g of lithium metaborate and 25 mg of lithium bromide, it was fused at 1200 °C for 20 minutes. The calibrations were validated regularly by analysis of reference materials, and 130 certified reference materials were used for the correction procedures. Due to the importance of accurate determination of the total Cr content of the waste, two different total digestion methods were evaluated.

Digestions

For the pressure bomb digestion, 0.05 g of hand-ground samples was weighed into polytetrafluoroethylene (PTFE) liner and mixed with HF, $HClO_4$, and HNO_3 (2:1:1 vol., concentrated, Suprapur, Merck). The acid mixture was heated slowly during five hours to 160 °C and then left at this temperature for 50 hours. After cooling, the samples were evaporated twice at 180 °C on a heating plate and then made up to a final volume of 50 mL with deionized water. Because the COPR was not totally dissolved, a second pressure bomb digestion with finer material was implemented. Therefore the samples were ground with cyclohexane for 5 minutes with a McCrone micronizing mill using a corundum grinding set. Under these conditions the samples were completely dissolved. The chromite-containing reference materials SARM 8 (Mintex, South Africa), CHR-Bkg (GIT-IWG, Geostandards, France), and CHR-Pt+ (GIT-IWG, Geostandards, France) were run simultaneously for quality control.

Due to the complexity of the pressure bomb digestion, a modified total microwave digestion application was evaluated. For this purpose, 0.05 g of hand-ground material was weighed into PTFE liner and mixed with concentrated HNO_3 (Suprapur, Merck), concentrated H_3PO_4 (Pro Analysis, Merck), and concentrated HBF_4 (pure, AppliChem) (5:3:2 vol.). The mixture was heated to 180 °C within 7 minutes in a microwave (Ethos, MLS). Seven minutes later, the temperature reached 260 °C and was held for 2.5 hours. After cooling, the samples were filled up to a final volume of 50 mL with deionized water. Aluminum, calcium (COPR samples), Cr, Fe, Mg, and Mn were analyzed by flame atomic absorption spectrometry (AAS, iCE 3500, Thermo) with a nitrous oxide–acetylene flame at 309.3 nm (Al), 422.7 nm (Ca), 357.9 nm (Cr), 248.3 nm (Fe), 285.0 nm (Mg), and 279.5 nm (Mn). The use of this type of flame was essential due to the formation of hardly atomizing phosphate compounds. To overcome ionization interferences, 0.2% (m/v) Cs [CsCl $Al(NO_3)_3$ buffer solution according to Schuhknecht and Schinkel, Merck] was used as an ionization buffer, except for Al, where 0.2% m/v K (KCl, Merck) was used. Sodium and K were measured with an air–acetylene flame and an ionization buffer as described above at 589.0 (Na) and 766.5 nm (K). Silicon and Ca (reference materials) were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima 2, Horiba Scientific) due to their low concentrations.

For the aqua regia digestion, 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 were added. After microwave digestion, the samples were filtered through a quantitative filter (5 to 10 µm, VWR) and made up to a final volume of 50 mL with deionized water. Chromium was measured as described before.

Chromate extraction

For this purpose, 50 mL of the extraction solutions were added to 2.5 g of non-milled samples. In the case of step 1 and 2 reactions took place at room temperature, for step 3 at 85 °C and for step 4 at room temperature in a sonication bath (Haver USC 200, Haver & Boecker).

X-ray powder diffraction (XRD)

The samples were carefully pre-ground by hand in an agate mortar. Afterwards the samples were finely ground in a McCrone micronizing mill using a corundum grinding set. Isopropanol was used as a cooling agent during grinding; the grinding time was 5 minutes for each sample. The preparation for the measurements was done by frontloading in a steel sample holder. Phase identification was done by reference to patterns in the powder diffraction file database, which was released in 2001 (Table S1).

Scanning electron microscopy (SEM)

Samples of dried COPR were vacuum impregnated with a low viscosity epoxy resin for BSE imaging, qualitative and quantitative EDX analysis, and element mapping. Afterwards, samples were polished with diamond paste up to 1 µm. Sections were coated with a thin layer (approx. 5 nm) of carbon to improve electrical conductivity. The contrast in BSE images from flat polished samples is determined by variations in average atomic number. Phases of a higher average atomic number are brighter than phases with a lower atomic number. Spectra for quantitative analyses were collected in the spot mode at intervals of 60 s using count rates of 10,000 counts s^{-1}. Spectra were then processed by a standardless-based ZAF correction. Initially, separate maps for each element were simultaneously recorded over a scan area of 512 × 400 points in the X and Y directions. A special software package (Genesis, Edax/Ametek) was applied to deduce phase maps from quantitative EDX maps for visualization of spatial distribution and relation of individual phases.

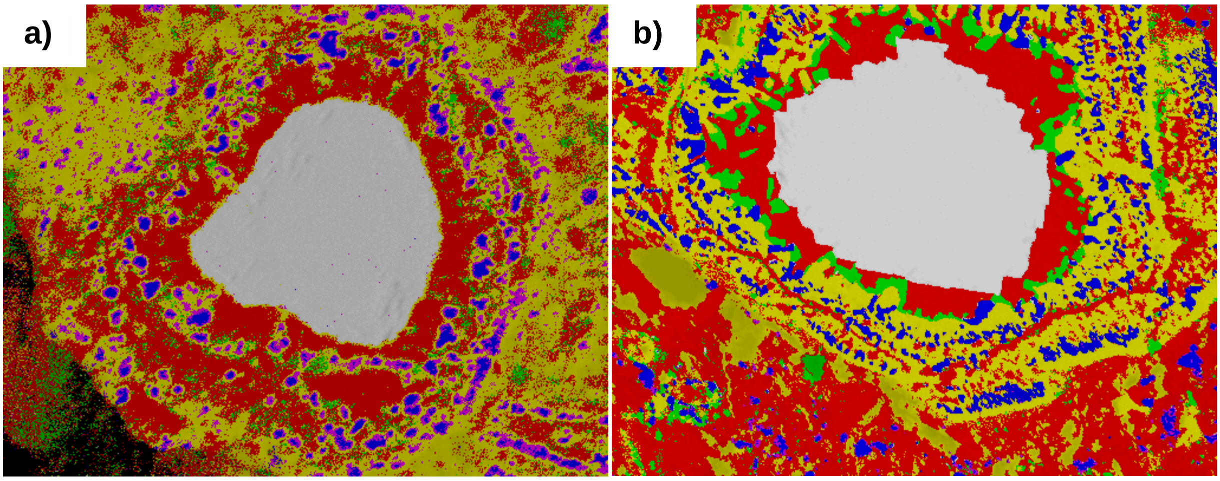

Fig. S1 Phase maps of COPR obtained from (a) Rania and (b) Chhiwali with the spatial distribution of the main mineral phases (white: magnesiochromite; red: CAC (Cr-rich); green: brownmillerite (Cr-poor); blue: periclase; pink: brucite; yellow: CAC phases (Cr-poor, Fe-rich).

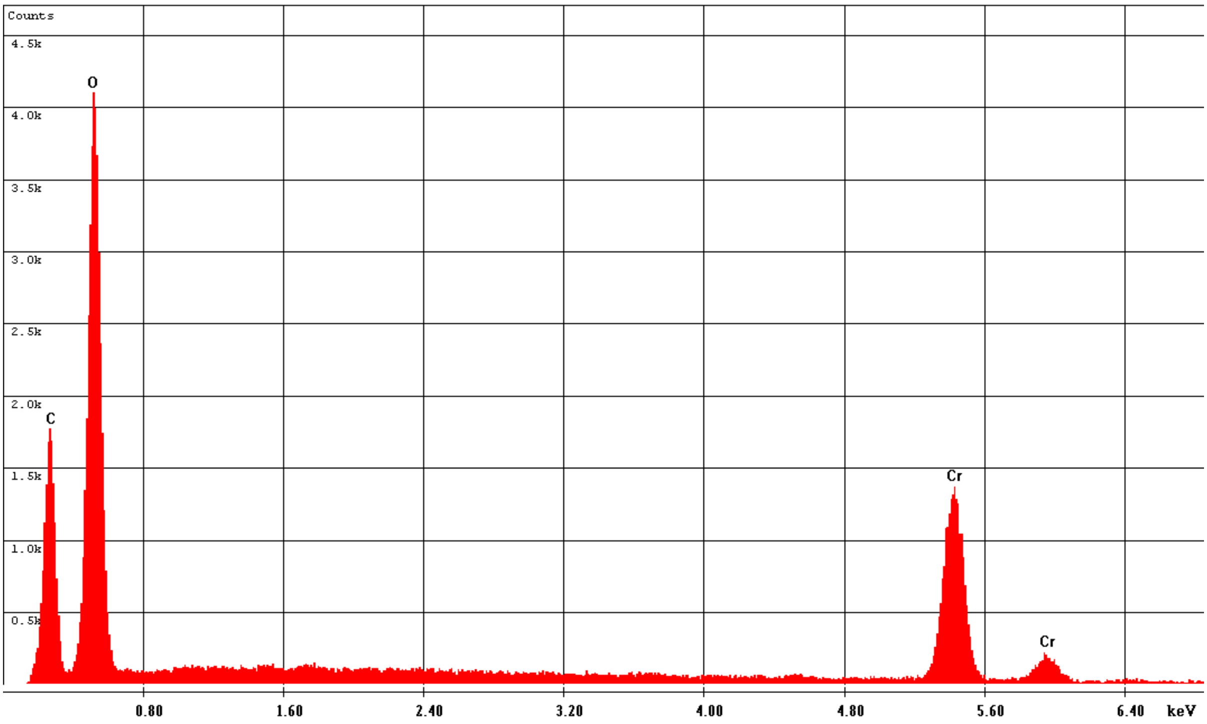

Fig. S2 Energy-dispersive X-ray spectrometer analyses of grimaldiite crystals in the Chhiwali COPR.

Table S1 Minerals identified in COPR using X-ray powder diffraction, backscattered electron images, and secondary electron images.

Mineral	Symbol	Chemical formula	PDF	Rania	Chhiwali
Aragonite[a]	A	$CaCO_3$	41-1475	—	x
Brownmillerite	B	$Ca_2(Fe,Al)_2O_5$	30-0226	x	x
Brucite	Br	$Mg(OH)_2$	07-0239	x	x
Calcite	C	$CaCO_3$	05-0586	x	x
CAC-14[b]	CAC	$Ca_4Al_2O_6(CrO_4)\cdot14H_2O$	52-0654	x	x
Ettringite[a]	E	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O$	41-1451	x	—
Magnesiochro-	Cr	$MgCr_2O_4$	10-0351	x	x
Grimaldiite	G	$CrO(OH)$	85-1372	x	x
Katoite	K	$(CaO)_3Al_2O_3(H_2O)_6$	24-0217	x	x
Larnite	L	Ca_2SiO_4	33-0302	x	x
Periclase	P	MgO	87-0652	x	x
Portlandite	Pt	$Ca(OH)_2$	04-0733	x	x
Quartz	Q	SiO_2	46-1045	x	x
Sjogrenite	S	$(Mg_6Fe_2(OH)_{16})(CO_3)(H_2O)_4$	24-1091	x	—
Voltaite	V	$K_2Fe_5Fe_3Al(SO_4)_{12}(H_2O)_{18}$	71-0718	x	x

[a] Not identified by XRPD but by BSE and SEI

[b] CAC: Calcium aluminum chromium oxide hydrate

Table S2 Comparison of total element contents (g kg^{-1}) of two Indian COPR samples (Rania and Chhiwali) and three certified reference materials determined by microwave digestion, pressure bomb digestion, and X-ray fluorescence (XRF).

		Rania	Chhiwali	SARM 8	CHR-Bkg	CHR-Pt^{+}
Fe	Microwave digestion	72.8	82.4	137	94.5	91.0
	Pressure bomb digestion	72.3	80.5	137	94.7	95.2
	XRF	73.2	83.8	—[a]	—	—
	crv[b]			141	97.0	93.9
Al	Microwave digestion	43.1	49.2	53.3	67.2	38.5
	Pressure bomb	42.7	47.4	56.4	57.3	37.7
	XRF	44.3	48.8	—	—	—
	crv			55.6	66.2	37.0
Si	Microwave digestion	35.0	46.2	21.5	66.6	97.9
	Pressure bomb	<0.001[c]	<0.001	<0.001	<0.001	<0.001
	XRF	38.9	49.1	—	—	—
	crv			20.0	71.4	102
Ca	Microwave digestion	223	240	1.60	0.32	1.60
	Pressure bomb	236	221	1.56	0.41	1.73
	XRF	225	227	—	—	—
	crv			1.86	0.50	1.64
Mg	Microwave digestion	45.6	60.6	88.1	139	155
	Pressure bomb	50.7	57.1	92.6	132	171
	XRF	47.3	60.4	—	—	—
	crv			88.1	145	169
Mn	Microwave digestion	1.25	1.17	1.91	1.07	1.16
	Pressure bomb	1.28	1.16	1.94	0.96	1.16
	XRF	1.29	1.21	—	—	—
	crv			1.94	1.08	1.16
Na	Microwave digestion	4.37	7.07	—	—	—
	Pressure bomb	4.48	7.25	—	—	—
	XRF	4.37	6.88	—	—	—
	crv			n.c.[d]	n.c.	n.c.
K	Microwave digestion	0.65	0.99	—	—	—
	Pressure bomb	0.63	1.07	—	—	—
	XRF	0.67	1.00	—	—	—
	crv			n.c.	n.c.	n.c.

[a] Not determined

[b] Certified reference values

[c] Below detection limit

[d] n.c.: Not certified

Chapter 4 Leaching of hexavalent chromium from young chromite ore processing residue

Manuscript

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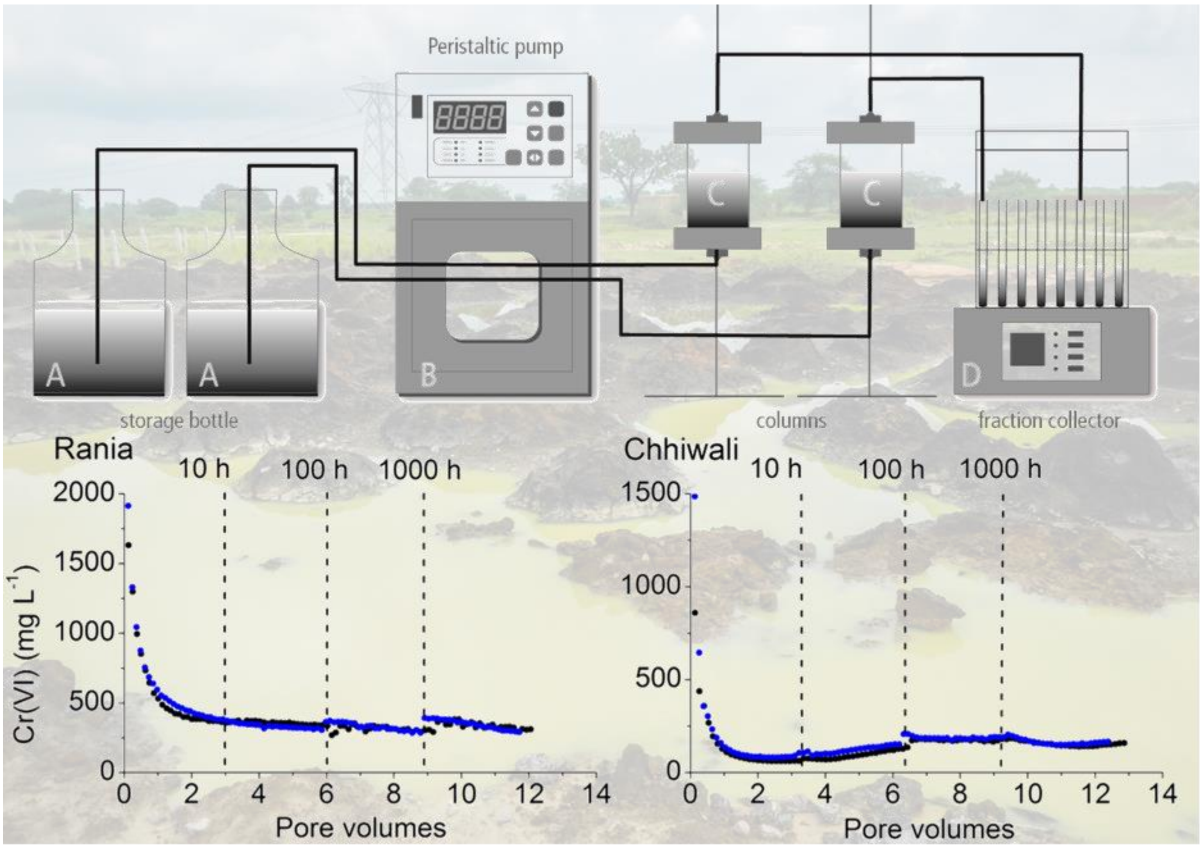
Graphical abstract



Highlights

- Cr(VI) was highly mobile in the COPR.
- Response to flow interruptions indicated equilibrium between solid and solution phases.
- Ratio of Cr(VI)/Cr_{total} decreased during column experiment.

Abstract

Chromite ore processing residue (COPR) is a waste derived from the chromate (CrO_4^{2-}) extraction from roasted ores, and is deposited in some countries in landfills. The objective of this study was to investigate the leaching characteristics of hexavalent Cr [Cr(VI)] from two COPR samples obtained from unlined landfills in the Kanpur area, Northern India. Column experiments were conducted under water-saturated conditions to simulate Cr release from the wastes caused by tropical heavy-rain events. Leached Cr(VI) decreased from 1800 mg L^{-1} to 300 mg L^{-1} (Rania site) and 1200 mg L^{-1} to 163 mg L^{-1} (Chhiwali site) during exchange of 12 pore volumes, which approximately corresponds to 2 years of monsoon precipitation. Flow interruptions for 10, 100 and 1000 h had little effect on Cr(VI) concentrations in the leachate, suggesting that Cr(VI) leaching was not limited by slow release kinetics. The results indicated that the solubility of Cr(VI) was dominated by highly soluble phases such as sodium chromate (Na_2CrO_4). Furthermore, mineral phases such as CAC-14 ($Ca_4Al_2O_6(CrO_4)\cdot 14H_2O$), Cr(VI)-ettringite ($Ca_6Al_2(OH)_{12}(CrO_4)_3\cdot 26H_2O$), and Cr(VI)-katoite ($Ca_3Al_2(CrO_4)_{0.12}(O_4H_4)_{2.88}$) controlled the solubility of Cr(VI) at experimental pH conditions. The amount of Cr(VI) leached from the columns accounted for 16% of the total Cr(VI) present in COPR in both samples. A decrease in the solid–phase Cr(VI)/Cr_{total} ratio along the column was identified by X-ray absorption near edge structure spectroscopy. Consistently, the smallest Cr(VI)/Cr_{total} ratios were found in the lower column section, where inflow took place. This indicates that mineral solubility controls aqueous Cr(VI) concentrations. Our results suggest that Cr(VI) leaching from the unlined COPR landfills will continue for a long time. Hence, remediation of these dumps should have highest priority to protect groundwater from Cr(VI) contamination.

Keywords

chromite ore processing residue (COPR); chromium; column experiment; leaching; speciation; X-ray absorption near edge structure spectroscopy

1. Introduction

High amounts of chromite ore processing residue (COPR) have been deposited in the environment in numerous industrial regions worldwide. The material is a waste stream derived from the extraction of chromate (CrO_4^{2-}) from ground and roasted chromite ores. In the roasting process, insoluble trivalent Cr [Cr(III)] present in the ores oxidizes to soluble hexavalent Cr [Cr(VI)], which is then recovered by aqueous leaching for further processing (Burke et al., 1991). The technology dates back to 1845 and is still in use in some emerging economies such as China, Russia, Kazakhstan, Pakistan, and India (Darrie, 2001).

Chromite ore processing residue contains unreacted chromite ore as well residual (i.e. non-extracted) CrO_4^{2-}. In general, COPR is strongly alkaline with pH values typically between 11.0 and 12.5 (Chrysochoou et al., 2009; Deakin et al., 2001b; Földi et al., 2013). Residual Cr contents of COPR range from 20 to 100 g kg^{-1} (Farmer et al., 1999; Földi et al., 2013; Geelhoed et al., 2003), where the majority of Cr is present as Cr(III), mainly as unreacted chromite, but Cr(VI) can also be present in levels of up to 30% (Geelhoed et al., 2003).

The two oxidation states differ in their chemical properties, environmental behavior, and toxicity. While Cr(III) is relatively immobile in most environmental systems (Fendorf, 1995), Cr(VI) has a high solubility in soils, particularly under slightly acidic to moderately alkaline conditions (e.g. Matern and Mansfeldt, 2016a). Hexavalent chromium [Cr(VI)] is a well-known human lung carcinogen (Halasova et al., 2009; Holmes et al., 2008), has carcinogenic potential by oral exposure (Sun et al., 2015), and causes allergic contact dermatitis (Shelnutt et al., 2007). In contrast, Cr(III) is according to today’s knowledge an essential dietary micronutrient (Pechova and Pavlata, 2007).

After landfilling, COPR is not stable and undergoes weathering reactions resulting in destabilization and dissolution of Cr(VI)-bearing minerals (Chrysochoou et al., 2010; Geelhoed et al., 2002; Wazne et al., 2008). One consequence at COPR-affected sites are elevated Cr(VI) concentrations in ground and surface water which may even be visually discernible by the characteristic yellow color of samples (Farmer et al., 2002; Matern et al. 2016b).

This study focuses on two sites near Kanpur (Uttar Pradesh, North India), where COPR from local chromite ore processing plants was landfilled in the environment. The first site referred to in this paper is located in Rania to the west of Kanpur in the district of Kanpur Dehat. Here, a plant was in in operation from the late 1980s until 2005. The thereof-derived COPR heap covers an area of ~1 km^2 and contains ~30,000 Mg of waste (Jaiswal and Braun, 2010). The second site is in Chhiwali, southeast of Kanpur in the district of Fatehpur. Here, two still operating Cr works were established in 2004.

The Cr(VI)-contamination related to the dumpsites is multiple end evident from a variety of investigations. Concentrations of Cr(VI) up to 80 mg L^{-1} were found in piezometers close to the main dumpsite in Rania (Singh et al., 2013). Asides groundwater contamination, there is a risk of migration of Cr(VI) and contamination of nearby soils, which are predominantly under agricultural use. Matern and Mansfeldt (2016b) reported a Cr content of 0.54 g kg^{-1} in an agricultural field close to a COPR dumpsite, from which about 9% were present in the mobile or exchangeable form.

Although leaching of Cr(VI) from soils (Andjelkovic et al., 2012; Matern and Mansfeldt, 2016b; Weng et al., 1994) and COPR (Deakin et al., 2001a, 2001b; Geelhoed et al., 2002; Wazne et al., 2008; Yalcin and Ünlü, 2006) has been widely studied, the findings cannot be simply transferred to the Indian sites. This is due to that COPR mineralogy differs depending on (i) chromite ore composition, (ii) the extraction process, and (iii) landfilling conditions. For example, COPR is often mixed with indigenous soils at some landfills, which contrasts to the deposition as pure COPR. The landfilling itself can be in layers of different age or origin, or as mixed wastes. Moreover, (iv) the ambient conditions may be vary resulting in different weathering rates. The COPR investigated in this study are exposed to a humid subtropical climate with monsoon rainfall occurring from July to September. In contrast, previous studies have investigated COPR from sites located in the temperate climate zone, in which rainfall is abundant throughout the year. Finally, (v) the age of the COPR is different, since the Indian COPR are relatively young (< 25 years) compared to COPR landfills investigated in other studies (between at least 40 and 180 years).

The aim of the present study was to investigate the release and transport of Cr from two young Indian COPR sites. Column experiments under water-saturated conditions were conducted to simulate Cr release from the wastes as caused by tropical heavy-rain events. Additionally, the experimental design used in previous batch and column studies using COPR did not allow the detection of possible non-equilibrium release mechanisms of Cr(VI). Assessing the release and transport of Cr from the COPR waste material, however, is essential for the evaluation of environmental risk and appropriate remediation strategies.

2. Material and methods

2.1 Study site, sampling and sample characterization

The COPR were sampled from two abandoned, illegally operated landfills in Rania and Chhiwali. In Rania, surface COPR was taken with a spade from a 20-year-old landfill, which was not covered by any material but left exposed. In Chhiwali, COPR was obtained at the edge of a 10-year-old heap, which had a thickness of about 6 m and was covered by a 30-cm-thick quartz-rich sandy soil. The samples were manually homogenized, air dried, and sieved (< 2 mm). Subsamples were ground in an agate ball mill (PM 400, Retsch, Haan, Germany). The main physical, chemical and mineralogical properties of the COPR have been described in Matern et al. (2016a).

2.2 Column experiments

The column experiments were performed in duplicate with the homogenized COPR fraction <2 mm. Figure 1 shows the scheme of the experimental setup. The COPR material was packed into cylindrical columns made of polyvinyl chloride (PVC) (EMC, Erfurt, Germany) with a length (L) of 20 cm, an inner diameter of 4 cm. The inlet and outlet of the columns were capped with a polyethylene filter fleece (Terram 1000, Hüsker GmbH, Gescher, Germany). For saturation, the columns were upstream fed with a degassed solution at a flow rate Q = 0.51 cm^3 min^{-1} using a peristaltic pump (Ismatec MCP with a MS/CA 8-6 pump head, Ismatec Laboratoriumstechnik, Wertheim, Germany). The solution had the composition of typical monsoon rain water according to Berner and Berner (1996) (all concentrations in mg L^{-1}): Na^+ 0.47; K^+ 0.23; Mg^{2+} 0.23; Ca^{2+} 1.4; Cl^- 0.92; SO_4^{2-} 0.63.

The duration and intensity of irrigation was derived from the natural monsoon precipitation in this area. Two years of irrigation were simulated with a cumulative precipitation of 1400 mm. Altogether, four irrigation phases were conducted, in each of which half of the annual precipitation (i.e. 350 mm) was applied within 24 h. Considering the cross-sectional area of the columns, this resulted in a flow rate of 18.33 mL h^{-1}. Between irrigation periods flow interruptions of increasing duration served to investigate whether Cr release under irrigation was rate-limited. The duration of each flow interruption differed by a factor of 10 (10 h; 100 h; 1000 h), which is sufficient for the detection of rate-limited processes (Wehrer and Totsche, 2003). The column effluents were sampled with two fraction collectors (SF-2120, Advantec, Dublin, USA and Thomachron-0/219, Reichelt, Heidelberg, Germany). Time-resolved sampling was performed in sampling intervals corresponding to 0.06 to 0.07 pore volumes (PV). To characterize the transport regime, a tracer breakthrough with Cl^- (0.01 M) was carried out after the irrigation cycles.

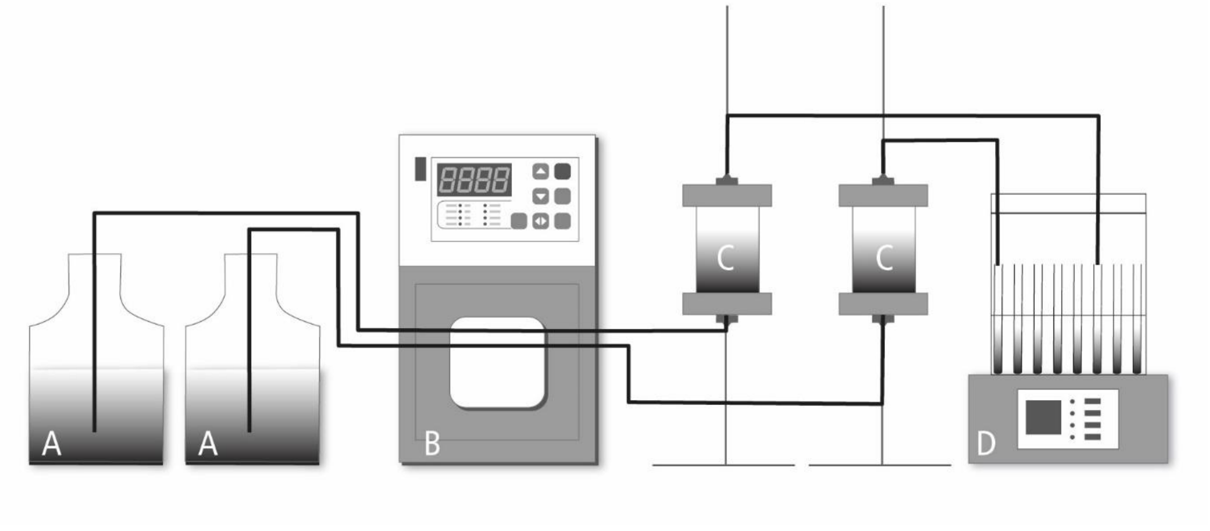


Fig. 1 Scheme of the experimental setup: A: storage bottle; B: peristaltic pump; C: column; D: fraction collector.

After the column experiments, the COPR material was removed in slices (~5 cm thick) from the columns and finely ground. Chromate was extracted with carbonate-hydroxide solution (0.28 M Na_2CO_3 in 0.5 M NaOH, pH 11.8 to12.3) according to James et al. (1995). For X-ray absorption spectroscopy (XAS) measurements, aliquots of the initial COPR materials and the COPR from the columns were mixed with a pre-calculated amount of boron nitride (BN) and pressed into pellets. Spectra were collected in transmission mode at the Cr K-edge on beamline SAMBA at the SOLEIL synchrotron (Saint Aubin, France). The Si(220) double crystal monochromator was calibrated against the edge-energy (first maximum of first derivative) of a Cr metal foil set to 5989 eV. The ion chamber detectors were filled with appropriate He/N_2 gas mixtures. The samples were cooled to ~30 K using a He cryostat to prevent beam-induced oxidation or reduction of Cr. Data reduction was done using the software Athena (Ravel and Newville, 2005).

2.3 Analyses of the COPR leachates

The solution pH was measured potentiometrically using a glass electrode (Unitrode, Methrom, Filderstadt, Germany). The electrical conductivity was determined using a conductivity electrode (SevenEasy, Mettler-Toledo, Gießen, Germany), and the ionic strength (I) was calculated according to Griffin and Juinak (1973), where σ is the electric conductivity in millisiemens per centimeter:

$$I = 0.013\ \sigma \qquad (1)$$

The above mentioned measurements were done directly after sampling to avoid CO_2 uptake from the atmosphere due to the high solution pH.

Chromium (VI) concentrations in the effluent were determined spectrophotometrically at 540 nm (Lambda 25 UV/Vis spectrometer, PerkinElmer) after reaction with diphenylcarbazide according to US EPA (1992). The concentrations of Ca, K, and Na were measured by flame atomic absorption spectrometry (AAS, iCE 3500, Thermo Scientific) with an air-acetylene flame and Cr was quantified by AAS with a nitrous oxide-acetylene flame. Chromium(III) concentration was calculated as the difference between total Cr and Cr(VI). Aluminum, Fe, Mg and Si were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima 2, Horiba Scientific, Unterhaching, Germany). Aqueous concentrations of F^-, Cl^-, NO_3^-, and SO_4^{2-} were determined by ion chromatography (ICS-1000, Dionex, Idstein, Germany).

2.4 Column data analyses

Bulk density (p_b) was calculated from the dry weight of the packed bed divided by the void volume V_0 of the column. The PV was obtained from bulk density and substance density (p_s) as 1 - p_b/p_s using the substance density of quartz (2.65 g cm^{-3}). Given saturated flow conditions the volumetric water content (θ) equals PV. Mean porewater velocity (v_{eff}) was obtained from the flow rate (Q) ($v_{eff} = Q/(A \times \theta)$), where A is the cross sectional area of the column. Normalized tracer concentrations (C/C_0) were obtained by the ratio of effluent and influent concentrations. Dimensionless time (number of PV eluted) was obtained by dividing the cumulative volume of effluent by the resident water volume.

The numerical code CXTFIT 2.1 (Toride et al., 1995) was used to determine the dispersion coefficient (D) and the retardation factor (R) by fitting the advection–dispersion equation to the chloride breakthrough data. Dispersivity (λ) is then given by D/v.

2.5. Geochemical modeling

The geochemical equilibrium modelling program Visual Minteq 3.0 was used for the calculation of the solubility of solid phases, which had been previously identified in COPR samples (Matern et al., 2016a). Therefore, activity coefficients were calculated with the Davies equation, which is valid for I <0.5 mol L^{-1} (Pankow, 1991). The solid phase thermodynamic database of Visual Minteq was complemented with thermodynamic data of the relevant solid phases cited from the literature (Table 1). In lack of a dedicated log K_{SP} for CAC-14, the log K_{SP} for CAC-12 was chosen according to Perkins and Palmer (2001).

3. Results and discussion

3.1 Column experiment and modelling

Table S1 summarizes the experimental conditions of the Cl^- breakthrough experiments and fitted parameters. Columns filled with Chhiwali COPR were more densely packed compared to the columns with the Rania COPR, but in both cases the duplicates were very similar to each other, resulting in similar ρ_b. Hence, the average values of θ and *PV* were slightly higher for the Rania columns. Figure S1 of the supplementary material (SM) shows the Cl^- breakthrough curves. Tracer breakthrough curves were symmetrical, indicating physical equilibrium and the absence of preferential flow. In nature, physical non-equilibrium due to heterogeneous flow conditions (preferential flow paths) is likely to control COPR leaching. This is due to a relatively broad aggregate size distribution (Geelhoed et al., 2003) caused by cementing and agglomeration (Dermatas et al., 2006). Hence, our experiments provide a worst-case approach by maximizing the contact surface of the waste with the aqueous phase. Fitting the chloride breakthrough data to the advection-dispersion equation was highly significant with r^2 ranging from 0.99 to 1.00. The dispersion coefficient, D, ranged from 0.01 to 0.03 cm^2 min^{-1}, resulting in dispersivities, λ, ranging from 0.21 to 0.56 cm. The column Peclet numbers, *Pe*, ranged from 36 to 95, indicating that the flow regime was advection-dominated. As can be seen from the retardation factors, *R*, which ranged from 1.4 to 1.6, Cl^- was not a conservative tracer but slightly retarded by the COPR material.

3.2. COPR leaching behavior

Overall leaching behavior. Figures 2 and 3 show the results of the COPR leaching behavior as a function of the number of pore volumes exchanged (dimensionless time). Aqueous concentrations of Al, Cr(III), Fe, Mg, and Si are not shown, since their concentrations were very low (Fe, Mg, and Si were below the limit of determination = 10 µg L^{-1}).

During leaching, the pH decreased moderately from 12.3 to 11.7 (Rania COPR) and 12.6 to 12.1 (Chhiwali COPR). This indicates a high buffer capacity of the COPR and suggests that alkaline pH values are likely to characterize the seepage water from COPR dumps in the next decades. The course of the ionic strength (estimated from the EC) was similar for both COPR. Starting from values of around 120 mmol L^{-1} the ionic strength decreased exponentially and levelled off at values of 30 mmol L^{-1} (Rania COPR) and 40 mmol (Chhiwali COPR) after exchange of 6 PV. Thus, a highly mobile pool of COPR constituents was leached out rather quickly (6 PV correspond to one year of precipitation) while comparably high base level concentrations were maintained by a further pool. The time series of the individual analytes show that the ionic strength was primarily influenced by Ca^{2+}, CrO_4^{2-}, and Na^+, while SO_4^{2-}, Cl^-, and K^+ contributed marginally. Leaching characteristics of the individual components differed, i.e., steady-state levels of Cr(VI) and Ca were attained after exchange of 3 PV, while Na approximated base level concentrations after 6 PV in both COPR.

Hexavalent chromium was truly a major solution phase component in the COPR leachates. This holds for both the leaching maxima and the base levels. The Cr(VI) concentration in the leachate decreased from 1800 mg L^{-1} to 300 mg L^{-1} in the Rania COPR and from 1200 mg L^{-1} to 163 mg L^{-1} in the Chhiwali COPR during 12 PV (2 years of monsoon precipitation). These Cr(VI) concentrations are 4 to 5 orders of magnitude above the WHO drinking water standard of 0.05 mg L^{-1} (WHO, 2011). Compared to Geelhoed et al. (2003), who leached COPR material from Glasgow, the Cr(VI) concentrations in leachates were around 50-fold higher in our study. Integration of the leaching curves indicated that 37% (Rania COR) and 28% (Chhiwali COPR) of the overall leached mass was released during the first 3 PVs. This is attributed to a highly mobile contaminant pool that is transferred into porewater during column saturation and then displaced by the uncontaminated influent. Conversely, the plateau values of Cr(VI) approximated after around 3 PVs result from the steady-state release driven by the amount of Cr(VI) mobilizable under the specific flow conditions.

Response to flow interruptions. To investigate whether release kinetics controlled COPR leaching, three consecutive flow interruptions of increasing duration (10h, 100h and 1000h) were performed (Fig. 2 and 3). Under continuous leaching, the porewater residence times (7.5 h and 8.2 h depending on bulk densities) are given by the ratio of porewater volume and flow rate. Since flow interruptions increase the porewater residence times effluent concentrations should increase when contaminant release is rate-limited.

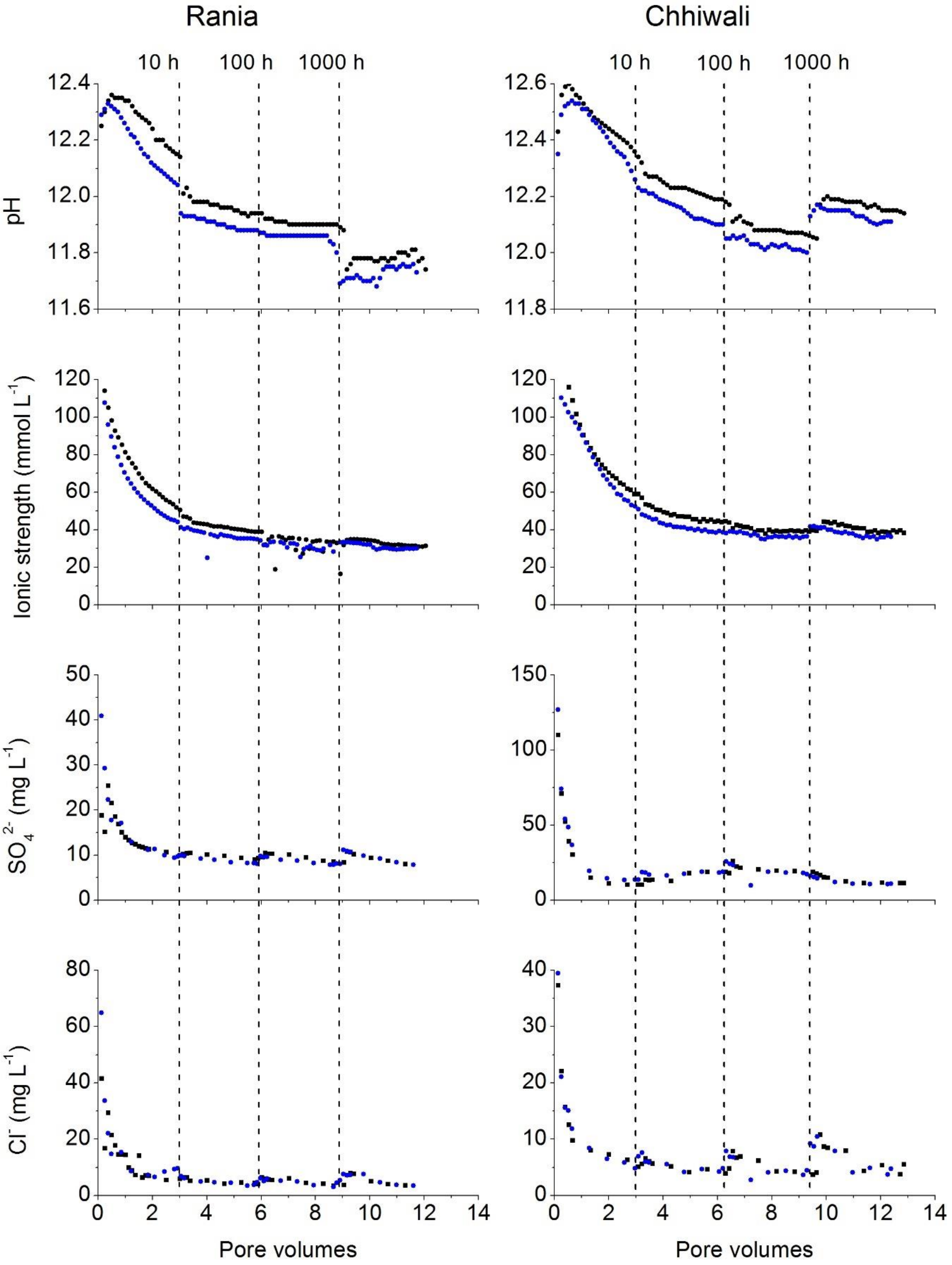


Fig. 2 pH, ionic strength, and aqueous concentrations of SO_4^{2-}, and Cl^- in the COPR column effluents (black, column A; blue, column B). Dashed lines indicate flow interruptions with duration of 10 h, 100 h, and 1000 h.

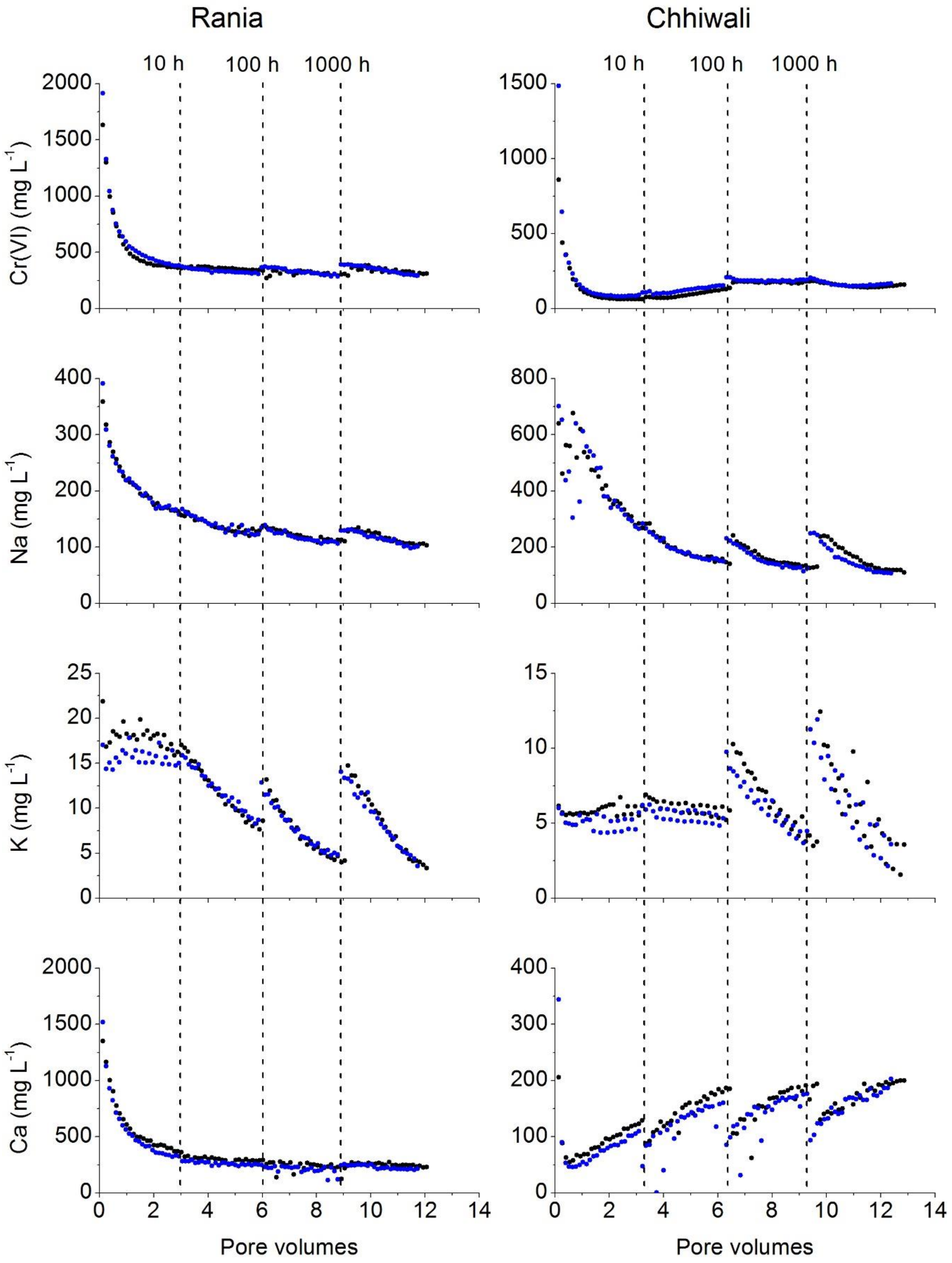


Fig. 3 Aqueous concentration of Cr(VI), Na, K, and Ca in column experiments with COPR (black, column A; blue, column B). Dashed lines indicate flow interruptions with duration of 10 h, 100 h, and 1000 h.

Our results show that Cr(VI) concentrations responded only very moderately to the flow interruptions. Thus, base level concentrations can predominantly be attributed to equilibrium between solid and solution phases. This is not the case for Na (Chhiwali COPR) and K (both COPRs). Here, the second and third flow interruptions caused a prominent increase of effluent concentrations pointing to rate-limited release. A different pattern was observed for Ca in the Chhiwali COPR where flow interruptions led to an initial decrease of the effluent concentrations with resumed percolation followed by a concentration rebound. Apparently, in this case flow conditions enhanced mobilization whereas increased residence times favored retention.

3.3. Possible solubility-controlling phases in COPR

Table S2 shows the solid phases identified in both COPR by X-ray powder diffraction (XRD) spectroscopy in a previous study. The high pH of the leachate is primarily determined by the dissolution of alkaline earth metals hydroxides that are present in COPR. Portlandite is formed rapidly upon hydration of excess quicklime (additive used in the high temperature roasting process) during the early stages of transport and landfilling (Chrysochoou et al., 2010). In the column experiments the initial effluent pH indicated that buffering is controlled by dissolution of portlandite (pH ~ 12.4), which was also observed in a drainage ditch of COPR in the north west of England (Deakin et al., 2001a). However, the role of portlandite seems controversial since Geelhoed et al. (2002) stated that the pH of COPR was not caused by the presence of portlandite and that the pH behavior cannot be explained by the presence of hydroxide and carbonate phases.

Solid phases, which were identified in the COPR by XRD or scanning electron microscopy (SEM) and may potentially play a role in controlling the Cr(VI) concentration in the leachates are sjogrenite, Cr(VI)-ettringite, calcium aluminum chromium oxide hydrate (CAC), Cr(V)-bearing katoite, and chromates of the alkaline and alkaline earth metals.

Sjogrenite is structurally related to CAC and is able to substitute Cr in the mineral structure or to retain CrO_4^{2-} in the interlayer. Wazne et al. (2008) reported that hydrotalcite my control the solubility of Cr(VI) through anion exchange. However, sjogrenite was only present in low contents in the Rania sample, and Mg as well as Fe concentrations in the leachates were below the limit of determination. Thus, its importance for controlling the Cr(VI) concentration in the leachate is negligible.

Ettringite is a hydration product of brownmillerite that may substitute CrO_4^{2-} for SO_4^{2-}. It was only detected in the Rania COPR via SEM (Matern et al., 2016a). Energy-dispersive X-ray (EDX) analyses indicated CrO_4^{2-} substitution in ettringite crystals. Due to the difficulty of the detection of ettringite with XRD (Matern et al., 2016a), the presence of ettringite in the Chhiwali COPR cannot be excluded. The log IAP of Cr(VI)-ettringite varied from 55.84 to 61.22 for the Rania COPR leachate and 52.77 to 56.56 for the Chhiwali COPR leachate (Table 1), which is in the range of values reported by (Geelhoed et al., 2002). Chrysochoou and Dermatas (2006) showed that Cr(VI)-ettringite was only stable between a pH of 10.9 and 11.18, whereas other studies reported a stability between pH 10.5 and 12.5 (Perkins and Palmer, 2000).

Table 1. Relevant solid phases for Cr(VI) leaching with their thermodynamics solubility constants (log K_{sp}) reported in the literature and the range of calculated log IAP and SI of the column leachates.

Solid phase	Solubility reaction	log K_{SP}	Range of calculated log IAP		SI	
			Rania	Chhiwali	Rania	Chhiwali
CAC-14	$Ca_4Al_2O_6(CrO_4){\cdot}14H_2O_{(s)} + 12H^+ \rightarrow 4Ca^{2+} + 2Al^{3+} + CrO_4^{2-} + 20H_2O$	71.02†	66.80 to 70.54	64.67 to 68.32	-4.22 to -0.48	-6.35 to -2.7
Calcium chromate	$CaCrO_{4(s)} \rightarrow Ca^{2+} + CrO_4^{2-}$	–2.27‡	-5.48 to -4.55	-6.52 to -5.42	-7.75 to -6.82	-8.79 to -4.55
Cr(VI)-ettringite	$Ca_6Al_2(OH)_{12}(CrO_4)_3{\cdot}26H_2O_{(s)} + 12H^+ \rightarrow 6Ca^{2+} + 2Al^{3+} + 3CrO_4^{2-} + 38H_2O$	60.29‡	55.84 to 61.22	52.77 to 56.56	-4.45 to 0.93	-7.52 to -3.73
Cr(VI)-katoite	$Ca_3Al_2(CrO_4)_{0.12}(O_4H_4)_{2.88(s)} + 11.52H^+ \rightarrow 3Ca^{2+} + 2Al^{3+} + 0.12CrO_4^{2-} + 11.52H_2O$	65.4$	-216.3 to -203.3	-222.7 to -211.0	-281.7 to -268.7	-288.1 to -276.4
Sodium chromate	$Na_2CrO_{4(s)} \rightarrow 2Na^+ + CrO_4^{2-}$	2.93‡	-7.56 to -6.16	-7.81 to -5.71	-10.46 to -9.09	-10.74 to -8.64

‡ Visual Minteq 3.0 database

† Perkins and Palmer (2001)

$ Geelhoed et al. (2002)

CAC-14 is isostructural with hydrocalumite and is a layered double hydroxide mineral known to have a high anion exchange capacity with CrO_4^{2-} anions held in the interlayers (Palmer, 2000; Wazne et al., 2008). Cr(VI)-katoite, often referred to as hydrogarnet is a hydration product of brownmillerite and able to substitute Cr(VI) in its tetrahedral structure (Hillier et al., 2007; Hillier et al., 2003). Both CAC-14 and Cr(VI)-katoite are major minerals identified in the investigated COPR. The observed log IAP of CAC-14 in the Rania COPR leachate varied from 66.80 to 70.54 and for the Chhiwali COPR leachate from 64.67 to 68.32 during the course of leaching. Except for one sample at the beginning of leaching, the log IAPs are altogether lower than the log K_{SP} of 71.02 (Table 1). These values are in the range of log IAP observed in other leaching experiments (e.g. 68.3 at 11.7, Geelhoed et al., 2002). The effluent solutions of Rania COPR had log IAP values between -216.3 and -203.3 with respect to Cr(VI)-katoite, and those of Chhiwali COPR between -222.7 and -211.0 (Table 1), respectively. These low values arise from consideration of CrO_4^{2-} in the mineral structure. Log IAPs for the pure katoite are distinctly higher (72.3 to 75.2 for Rania and 72.7 to 74.7 for Chhiwali). However, the log IAP for substituted katoite depends strongly on the composition of the phase, which is also reflected by the differences in reported log K_{SP} values that range from 78.3 to 81.5 (Geelhoed et al., 2002). Modelling results of Geelhoed et al. (2002) indicated that Cr(VI) concentrations in the leachates can be accurately described assuming mineral equilibrium with Cr(VI)-ettringite, Cr(VI)-hydrocalumite and Cr(VI)-hydrogarnet for the pH range between 10 and 12, which is the case in our experiment. Wazne et al. (2008) concluded from leaching experiments that the COPR continuously leaches Cr(VI) at concentrations equivalent to the solubility Cr(VI)-hydrocalumite. This was also the case in experiments of Chrysochoou and Dermatas (2006), who reported that Cr(VI) bound in hydrocalumite was constant in the pH range of 11.3 and 12.4 and led to Cr(VI) leachate concentrations of below 50 mg L^{-1}. Geelhoed et al. (2002) reported Cr(VI) concentration of 20 mg L^{-1} at the equilibrium pH of COPR.

Due to the stability of Ca-Al phases down to pH 11 and Mg-Al phase down to pH 8 (Chrysochoou et al., 2009), the high Cr(VI) concentration in the leachates cannot simply be explained by the solubility control of the aforementioned mineral phases. In the Chhiwali COPR, easily soluble compounds such as Na_2CrO_4 and Na_2SO_4 were detected by SEM (Matern et al., 2016a). They were present in pores and thus, possibly protected from leaching on site. However, it is likely that easily soluble phases are also present in the Rania COPR due to the similar production processes, age of landfill and weathering conditions. For the Rania COPR, leaching characteristics of Cr(VI) and Na were quite similar while they differed for the Chhiwali COPR. Leachates of both samples were distinctly undersaturated with respect to $NaCrO_4$ with log IAP ranging from –6.2 to –7.6 for the Rania COPR and –5.7 to –7.8 for the Chhiwali COPR. To the best of our knowledge, dissolution of easily soluble Cr-containing phases combined with detection of the phase in the solid sample was not reported before. In a previous study of Breeze (1973) it was shown that Na and Cr leached in quantities, which could account for Na_2CrO_4. However, the sample was extracted with dilute acid which may significantly influence leaching behavior. Furthermore, Breeze (1973) pointed out that the CrO_4^{2-} in the waste is rather a mixed salt of more than one cation. James (1994) suggested that moderately soluble phases such as $CaCrO_4$ may be responsible for Cr(VI) leaching from COPR located in areas of Hudson County, New Jersey. The author detected crusts, which contained CrO_4^{2-} salts on the surface of poorly drained soils, at which evaporation took place. The log IAP with respect to $CaCrO_4$ ranged from –5.48 to –4.55 in the Rania leachate and from –6.52 to –5.42 in the Chhiwali leachate, which is in the range of log IAP reported in other studies (–6.5, Geelhoed et al., 2002; –4.6, Deakin et al., 2001). Although $CaCrO_4$ was not detected in the COPR used in our study, it's role as possible solubility-controlling phase cannot be excluded.

3.4. Extractable CrO_4^{2-} and Cr oxidation state in the COPR solid phase

Table 2 summarizes the extractable amounts of CrO_4^{2-} and the ratio of Cr(VI)/Cr_{total} in the COPR determined by X-ray absorption near edge structure (XANES) (Fig. 4 and Fig. S2). In the lower column section (feed side), the ratio Cr(VI)/Cr_{total} decreased. Since no Cr(III) was leached, this mirrors the depletion of solid phase Cr(VI) by leaching. The XANES results gives a cumulative Cr(VI) export of 2.7 g kg^{-1} for the Rania COPR and 1.5 g kg^{-1} for the Chhiwali COPR, (equivalent to 16% of the initial Cr(VI). The depth dependence of the Cr(VI) depletion indicated by XANES is confirmed by the Cr(VI) extractions of the solid phase after the column experiments. For both COPR samples, most of the Cr(VI) initially present was leached out in the lower (inflow) section of the columns. Extractions indicate, that altogether, the Cr(VI) content in the lower column section was reduced by about 38% in the Rania COPR and 40% in the Chhiwali COPR. In the upper column section, no Cr(VI) was leached out for the Rania COPR and a marginal amount of 3% for was leached in the Chhiwali COPR. These findings are consistent with the base level of Cr(VI) found in the leaching experiments. Since the reservoir of Cr(VI)-bearing mineral phases has obviously not been depleted within the course of 12 PV (i.e. the total duration of the experiments) effluent concentrations maintained a roughly constant value. Regarding field conditions and the thickness of the COPR dumps Cr(VI) leaching must be expected to continue for a long time with obvious consequences for downstream groundwater quality.

Table 2 Cr(VI) concentration extracted with a carbonate-hydroxide solution (0.28 M Na_2CO_3 in 0.5 M NaOH) according to James et al. (1995) and solid-phase Cr(VI)/Cr_{total} fractions in column sections at the end of the column leaching experiments as estimated from the pre-peak intensity of Cr K-edge XANES spectra (Figure S3).

Depth	Rania		Chhiwali	
(cm)	(g kg^{-1})	Cr(VI)/Cr_{total}	(g kg^{-1})	Cr(VI)/Cr_{total}
0-3	16.4	0.39	8.9	0.19
3-10	14.7	0.38	8.4	0.22
10-17	13.4	0.35	7.5	0.17
17-20	10.2	0.31	5.5	0.17
$\bar{x}$†	13.8		7.7	

†Cr(VI) contents before column experiment were 16.5 g kg^{-1} (Rania) and 9.2 g kg^{-1} (Chhiwali).

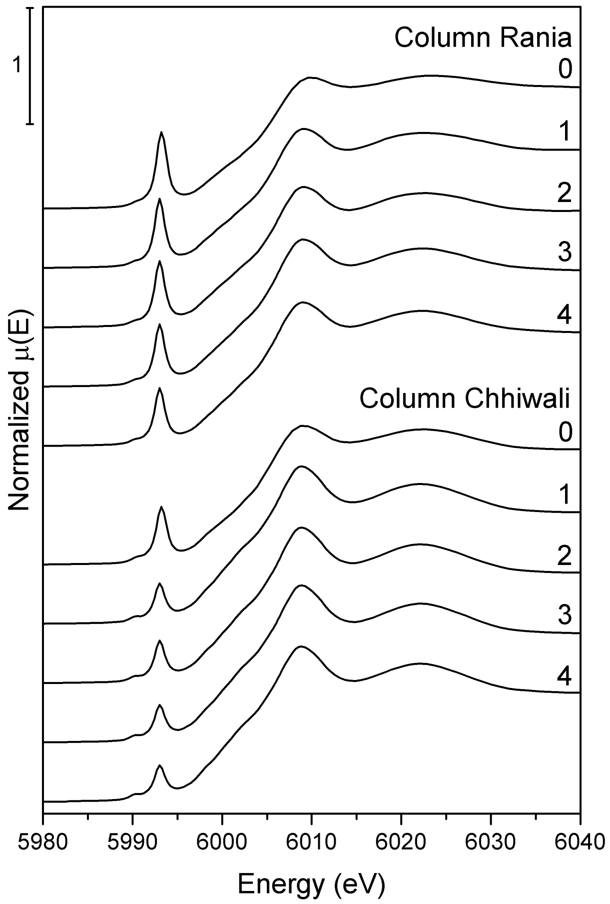


Fig. 4 Normalized Cr K-edge XANES spectra of leached COPR materials from Rania and Chhiwali, respectively. The pre-peak intensity at 5993 eV was used to estimate the Cr(VI)/Crtotal ratios reported in Table 2.

4. Conclusions

The leaching behavior of Cr(VI) was investigated in soil column experiments. Experimental results indicated that Cr(VI) is highly leachable in both COPR and forms a major solution component. Highly soluble phases such as Na_2CrO_4 were identified as a main source of Cr(VI). However, it is likely that Cr(VI)-ettringite, CAC-14 and Cr(VI)-katoite, which are main constituents of the COPR, also control aqueous Cr(VI) concentration through CrO_4^{2-} exchange. In this context and assuming equilibrium with theses minerals, it is expected that Cr(VI) may be continuously leached from the waste, as far as pH conditions do not change. Since the latter can be expected from very high buffering capacity of the investigated COPR, long-term inputs into the aquifers of the study sites can be expected to be around the observed base-levels of the leaching curves (i.e. between 100 and 300 mg L^{-1}). Quantitative XRD analyses of the solid phase before and after column experiments may be helpful to verify the experimental results reported here. Altogether it can be assumed that leaching of high Cr(VI) concentration will continue for a long time. Thus, asides well water treatment and ground water remediation a removal or stabilization of the COPR dumpsites is mandatory.

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Supplementary material

Leaching of hexavalent chromium from young chromite ore processing residue

Table S1 Experimental parameters of Cl^- breakthrough curves in COPR and results of fitting the breakthrough data to the advection-dispersion equation (Equation (3)) using CXTFIT 2.1. The parameters R and D were fitted.

Parameter^s	Unit	Rania		Chhiwali	
		column A	column B	column A	column B
L	(cm)	20	20	20	20
A	(cm^2)	12.6	12.6	12.6	12.6
p_b	($g\ cm^{-3}$)	1.05	1.04	1.22	1.22
θ	($cm^3\ cm^{-3}$)	0.60	0.61	0.54	0.54
PV	(cm^3)	150.2	146.0	136.8	142.1
Q	($cm^3\ min^{-1}$)	0.31	0.31	0.31	0.31
q	($cm\ min^{-1}$)	0.024	0.024	0.024	0.024
v_{eff}	($cm\ min^{-1}$)	0.040	0.040	0.045	0.045
pv	(–)	0.0020	0.0020	0.0022	0.0023
D	($cm^2\ min^{-1}$)	0.01	0.01	0.03	0.02
λ	(cm)	0.21	0.32	0.56	0.37
Pe	(–)	95	62	36	54
R	(–)	1.5	1.6	1.4	1.4
r^2	(–)	1.00	0.99	0.99	0.99

L, length of the column; A, cross sectional area; p_b, bulk density; θ, volumetric water content; PV, pore volume; Q, flow rate; q, Darcy flux; v_{eff}, pore water velocity; pv, reduced time; D, dispersion coefficient; λ, dispersivity; Pe, column Peclet number; R, retardation factor; r^2, square of the correlation coefficient.

Table S2 Solid phases identified in COPR (Matern et al., 2016).

solid phase	chemical formula	Rania	Chhiwali
aragonite	$CaCO_3$	—[†]	x
brownmillerite	$Ca_2(Fe,Al)_2O_5$	x	x
brucite	$Mg(OH)_2$	x	x
CAC-14	$Ca_4Al_2O_6(CrO_4)\cdot 14H_2O$	x	x
calcite	$CaCO_3$	x	x
Cr(VI)-ettringite	$Ca_6Al_2(CrO_4)_3(OH)_{12}\cdot 26H_2O$	x	—
katoite	$(CaO)_3Al_2O_3(H_2O)_6$	x	x
ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$	x	—
grimaldiite	$CrO(OH)$	x	x
magnesiochromite	$MgCr_2O_4$	x	x
periclase	MgO	x	x
portlandite	$Ca(OH)_2$	x	x
sjogrenite	$(Mg_6Fe_2(OH)_{16})(CO_3)(H_2O)_4$	x	—
sodium chromate	Na_2CrO_4	—	x
voltaite	$K_2Fe_5Fe_3Al(SO_4)_{12}(H_2O)_{18}$	x	x

† not detected

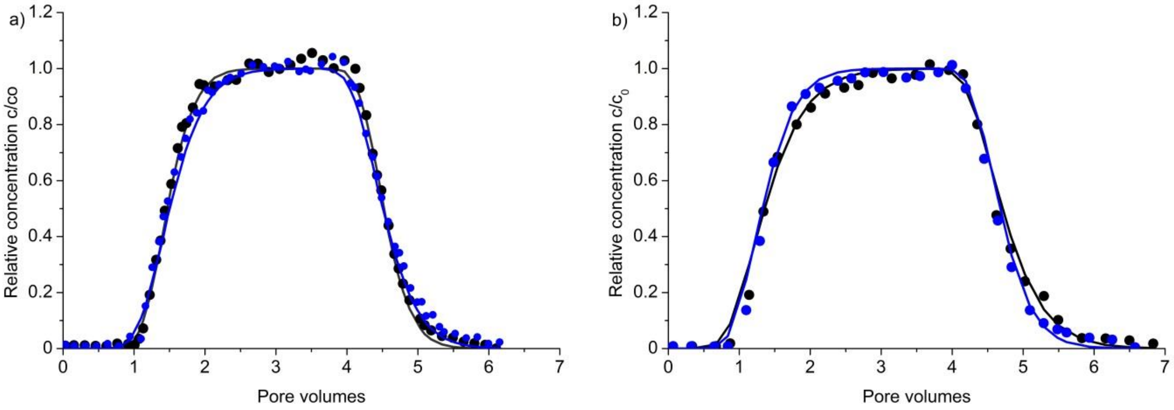

Fig. S1 Breakthrough curves of chloride in a) in Rania COPR and b) in Chhiwali COPR. Symbols indicate measured data (black, column A; blue, column B), and the lines result from fitting the advection–dispersion equation to the chloride breakthrough data using CXTFIT.

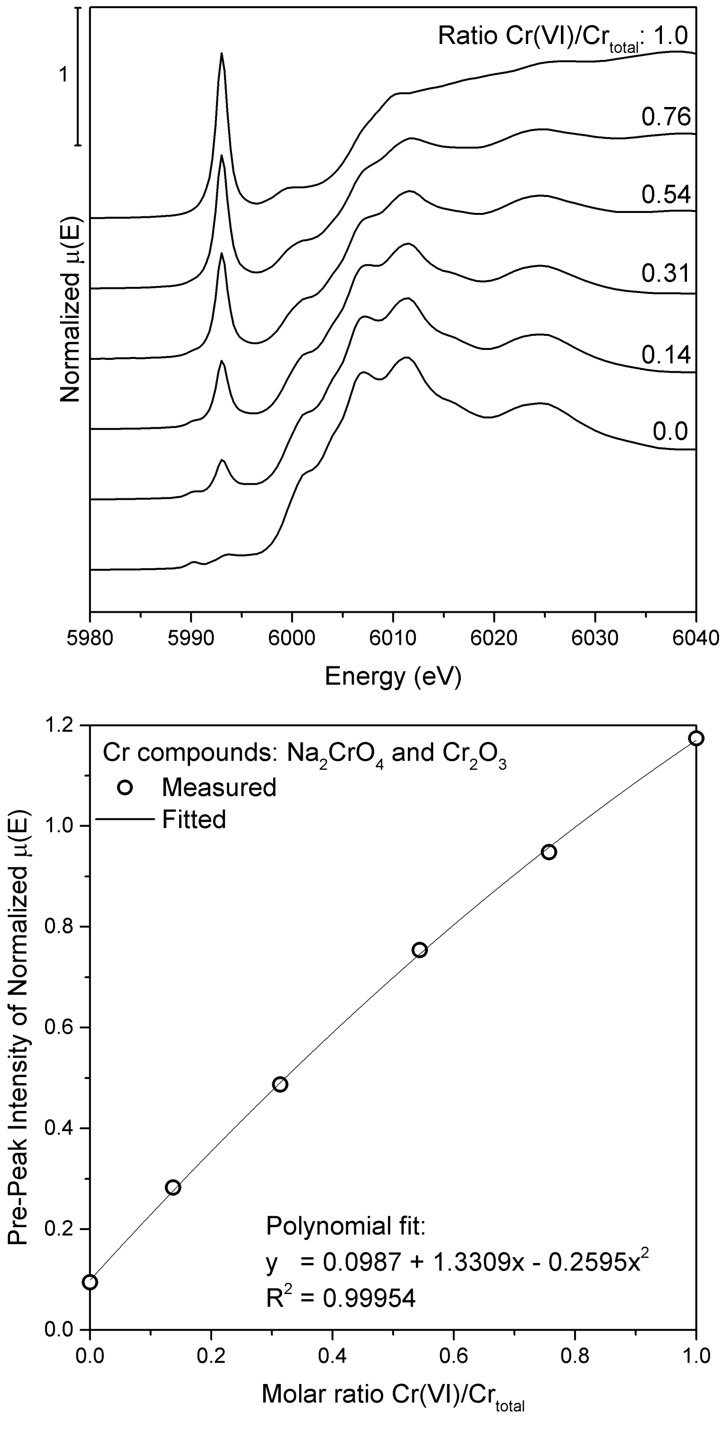

Fig. S2 (a) Normalized Cr K-edge XANES spectra of Na_2CrO_4 ($Cr(VI)/Cr_{total}=1$), Cr_2O_3 ($Cr(VI)/Cr_{total}=0$), and four physical mixtures of both reference compounds with estimated $Cr(VI)/Cr_{total}$ ratios of 0.76, 0.54, 0.31, and 0.14, respectively. (b) Linear correlation between the $Cr(VI)/Cr_{total}$ ratio and the pre-peak (5993 eV) intensity of normalized XANES spectra.

Chapter 5 Chromate adsorption from chromite ore processing residue eluates by three Indian soils

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Formatting and orthography is according to the dissertation style

Environmental context

Chromate (CrO_4^{2-})-containing waste is illegally dumped in some places in the state of Uttar Pradesh, north India, although CrO_4^{2-} is known to be toxic and carcinogenic. Because CrO_4^{2-} is leached from the landfills, this study investigated the adsorption of CrO_4^{2-} by soils. The results indicated that CrO_4^{2-} is highly leachable and adsorption is inhibited, which leads to contamination of the groundwater and drinking water in this area.

Abstract

Chromite ore processing residue (COPR) is a harmful waste of the chromate (CrO_4^{2-}) extraction roasting process. Nevertheless, deposition of COPR in uncontrolled surface landfills is still common practice in some countries. Leaching of carcinogenic CrO_4^{2-} and contamination of groundwater is a key environmental risk arising from COPR sites. The objective of this study was to evaluate the adsorption behaviour of CrO_4^{2-} from COPR eluates by soils. Prior to the adsorption experiments, batch studies at varying solid-to-liquid ratios were performed to evaluate the solubility of CrO_4^{2-} from COPR. Chromate adsorption experiments were carried out in a batch system with eluates obtained from two different Indian COPRs to assess potential groundwater contamination by CrO_4^{2-}. Three soils that originate from the surroundings of COPR dumping sites were chosen in order to provide realistic adsorption conditions. The data were evaluated with the Freundlich and Langmuir equation. Chromate adsorption was inhibited because of the high pH of both of the soils (pH 6.7 to 7.2) and the eluates (pH 12.3) as well as the high carbonate concentration of the eluates. The extent and behaviour of CrO_4^{2-} adsorption from both eluates was similar. The main difference between the eluates was the solubility of CrO_4^{2-} from COPR and thus the initial CrO_4^{2-} concentration. The results presented in this study provide an improved understanding of the mobility of CrO_4^{2-} in the affected area, which is important because the local population uses the groundwater not only for the needs of livestock but also as drinking water.

1. Introduction

Chromium is one of the most widely used elements in various industries such as metallurgy, electroplating, pigment production and leather tanning.[1] It is a redox-sensitive transition metal and typically occurs under environmental conditions in the trivalent (Cr^{III}) and hexavalent (Cr^{VI}) oxidation states. Thereby the oxidation state controls its chemical properties and environmental behaviour. Although Cr^{III} is, according to today's knowledge, an essential micronutrient for mammals,[2] Cr^{VI} is carcinogenic, principally when inhaled[3] but also when consumed from drinking water,[4] and causes allergic contact dermatitis.[5] Chromium compounds are also highly toxic to plants.[6] Because of its toxicity, the World Health Organization (WHO) has assigned a guideline value of 0.05 mg L^{-1} for total Cr in drinking water.[7]

Extensive Cr contamination occurs in the area of Kanpur in the State of Uttar Pradesh, north India, where there is a prominent cluster of leather-processing industries. The Cr^{III} salts used in leather tanning are produced in Rania, to the west of Kanpur in the district ofKanpur Dehat, and in Chhiwali, to the south-east of Kanpur in the district of Fatehpur. A high-lime processing technique is used to oxidise the Cr in the ore from the insoluble Cr^{III} to the soluble Cr^{VI}, followed by aqueous leaching.[3] This technique produces so-called chromite ore processing residue (COPR), which is found in landfill in the environment in large amounts. In Rania, Cr works were in operation from the late 1980s until 2005. One heap covers an area of ~1 km^2 and contains ~30 000 Mg of waste COPR.[8] In Chhiwali, two Cr works were established in 2004 and are still operating.

The COPRs are strongly alkaline, with pH values varying from 11 to 12.5.[9–11] Residual Cr contents of waste COPR range from 20 to 110 g kg^{-1},[11–13] of which up to 30 % is present as Cr^{VI}.[13] After deposition, COPR is not stable and undergoes weathering reactions, resulting in destabilisation and dissolution of Cr^{VI}-bearing minerals.[14–16]

The Cr^{VI} components contained in COPR form chromate (CrO_4^{2-}), an oxoanion, following release in the alkaline milieu of the COPR. However, the protonated CrO_4^{2-} species, $HCrO_4^-$, is also present in the surface environment at $pH < 6.6$.[17] For simplicity, we summarise all Cr species as chromate (CrO_4^{2-}) in the following. The adsorption of CrO_4^{2-} has been intensively studied with different soil components as a function of initial concentration, pH, ionic strength and competing anions.[18–28] Chromate is adsorbed by various mechanisms onto Al and Fe oxides, which commonly have a net positive charge and a potential chemical affinity for CrO_4^{2-}.[17] A spectroscopic investigation indicated that CrO_4^{2-} was able to form inner-sphere surface complexes via ligand exchange with surface hydroxy groups.[21,23,29] Modelling studies suggested that electrostatic adsorption also occurs and CrO_4^{2-} forms outer-sphere surface complexes.[18,19,30,31] Furthermore, the formation of weak surface complexes on kaolinite was observed.[32]

The extent of CrO_4^{2-} adsorption is highly correlated with pH, with an adsorption maximum at pH values close to the pK_{a1} of the conjugate acid, chromic acid, which is very low ($pK_{a1} = -0.2$[33]). Therefore, experimental data typically showed a decrease in CrO_4^{2-} adsorption with increasing pH.[27,29] Chromate adsorption is also affected by competing oxoanions, which significantly reduces the amount of adsorbed CrO_4^{2-}.[18,25,34]

Chromate adsorption is also influenced by ionic strength, because adsorption is determined by the electrostatic potential on the adsorption plane, which is, however, controlled by the ionic strength of the solution.[28] Thereby, outer-sphere surface complexes are more influenced by ionic strength than inner-sphere surface complexes, because the background electrolyte ions are placed in the same plane for outer-sphere surface complexes.[27] Moreover, CrO_4^{2-} adsorption is affected by high alkalinity, because of competition of carbonate ions for surface binding sites.[34] Furthermore, CrO_4^{2-} adsorption changes from inner-sphere to outer-sphere surface complexes with increasing carbonate concentration.[34] Overall, CrO_4^{2-} tends to have a high solubility in soils, particularly under slightly acid to alkaline conditions.[35,36]

The aim of the present study was to determine the adsorption behaviour of CrO_4^{2-} from COPR eluates in order to assess potential groundwater contamination by CrO_4^{2-} around dumping sites. The COPR used in the current study was obtained from Rania and Chhiwali, Uttar Pradesh. Indeed CrO_4^{2-} adsorption has been investigated on a wide range of soils and soil constituents. A major innovation of this research was the experimental design with COPR eluates as the background electrolyte, which may have a significant influence on adsorption because of their specific chemical composition. The results presented in this study provide an improved understanding of the mobility of CrO_4^{2-} in the affected area, which is important because the local population uses the groundwater not only for the needs of livestock and irrigation but also as drinking water.

2. Material and methods

2.1 Sampling sites and sample preparation

The COPRs were sampled from two abandoned illegally operating disposal sites in Rania and Chhiwali in the State of Uttar Pradesh. In Rania, homogeneous surface COPR was taken with a spade from 20-year-old landfill, which was not covered by any material but left exposed to the surface. In Chhiwali, COPR was obtained at the edge of a 10-year-old landfill which had a thickness of ~6 m and was covered by a 30-cm-thick layer of quartz sand. At both sites, the sampling depth was ~30 cm.

Altogether, Cr adsorption was investigated with three soils that were taken from locations near to the disposal sites, to obtain realistic conditions. One soil was obtained from an agricultural field in Rania (#1) and two were obtained from Chhiwali, of which one was a subsoil (#2) and the other was also sampled from an agricultural field (#3). Alluvial deposits of the Ganga, which are predominantly constituted of micaceous sand, silt and clay, were the parent material of the soils. The sampling depth at the agriculture field was 0 to 15 cm and the subsoil was sampled at a depth of 75 to 100 cm. The samples were manually homogenised, air-dried and sieved to <2 mm.

2.2 Characterisation of the soil samples

Particle size distribution was analysed by wet sieving and sedimentation using the pipette sampling technique. Prior to the analyses, soil organic matter was destroyed with H_2O_2 and carbonates were destroyed with HCl. Clay mineralogy was analysed by X-ray diffraction (XRD) on random powder samples ($Co_{K\alpha}$; Philips diffractometer PW 1070, PANalytical: Kassel, Germany). The measurement range was 5 to 80° 2θ with a step size of 0.02° 2θ and a counting time of 5 s for each step. Natural quartz present in the samples was taken as an internal standard to correct the 2θ position of each fitted peak. For the preparation of the measurement, the clay fraction was separated, saturated with Ca^{2+}, washed and freeze-dried. Afterwards, the samples were saturated with glycerol (room temperature) as well as K^+ (room temperature and heated stepwise to 20, 100, 400 and 560 °C). The results were evaluated with the fitting program *MacClayFit*.[37]

Soil pH was measured potentiometrically using a glass electrode (Unitrode, Metrohm: Filderstadt, Germany) in both 0.01 M $CaCl_2$ solution and deionised water with a solid to-solution ratio of 1:5. Total C and N were quantified with a CNS analyser (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_o) were determined according to Schwertmann[38] and dithionite-citrate extractable Fe (Fe_d) according to Mehra and Jackson.[39] The concentrations of Mn and Fe were measured by flame atomic absorption spectrometry (AAS, 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 polytetraflouroethylene (PTFE) liner. Concentrated HNO_3 (2 mL, Suprapur, Merck: Darmstadt, Germany) and concentrated HCl (6 mL, Suprapur, Merck: Darmstadt, Germany) were then added. After microwave digestion, the samples were filtered through a quantitative filter (5 to 10 µm, VWR: Darmstadt, Germany) and made up to a final volume of 50 mL with deionised water. Iron and Mn were measured as described before and Cr was determined by AAS with a nitrous oxide–acetylene flame.

2.3 Preparation and characteristics of the COPR eluates

To obtain knowledge about the Cr solubility as well as the aqueous Cr species present, simple batch experiments were performed. Samples were shaken with a solution of 0.01 M $CaCl_2$ for 24 h. Solid-to-liquid ratios were 1 : 2, 1 : 20, 1 : 200, 1 : 500, 1 : 1000, 1 : 5000, and 1 : 10 000 in order to obtain a quantitative dissolution. Fine particles were separated by centrifugation at 5000*g* at 20 °C for 10 min, followed by filtration (0.45 µm). The Cr^{VI} concentration in the eluates was determined spectrophotometrically at 550 nm (Lambda 25 UV/Vis spectrometer, Perkin–Elmer: Rodgau, Germany) with diphenylcarbazide[40] immediately after filtration, and total Cr was measured as described above. The Cr^{III} concentration was calculated as the difference between total Cr and Cr^{VI}.

For the preparation of the eluates, COPRs were leached by shaking for 24 h at a COPR-to-solution ratio of 1 : 2 followed by filtration (5 to 10 µm, VWR: Darmstadt, Germany). The solution used had the composition of typical monsoon rain water according to Berner and Berner[41] (all concentrations in milligram per litre): Na^+ 0.47; K^+ 0.23; Mg^{2+} 0.23; Ca^{2+} 1.4; Cl^- 0.92; SO_4^{2-} 0.63. This tight ratio was chosen to simulate the field conditions.

The eluate pH was measured potentiometrically using a glass electrode (Unitrode easyClean, Metrohm: Filderstadt, Germany). The electric conductivity was determined using a conductivity electrode (SevenEasy, Mettler-Toledo: Gießen, Germany), and the ionic strength (*I*) was calculated according to Griffin and Jurinak,[42] where σ is the electric conductivity in millisiemens per centimetre:

$$I = 0.013\sigma \qquad [1]$$

For the determination of alkalinity, 5 mL of the eluates was titrated with 0.1 M HCl to pH 8.2 and 4.3 using a Metrohm 775 Dosimat and a Metrohm 728 Stirrer. The concentrations of Ca, Cr, K and Na were measured by flame AAS with an air–acetylene flame and the concentrations of Al, Si, Sr, As, Ba, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, V, Sb, Se and Zn were measured by inductively coupled plasma–mass spectrometry (ICP-MS, X-Series II, Thermo Scientific: Dreieich, Germany). The Cr^{VI} concentration in the eluates was determined as described above. The concentrations of F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_2^- and NO_3^- were determined by ion chromatography (ICS-1000, Dionex: Idstein, Germany).

2.4 Adsorption experiments

Adsorption experiments were performed with the COPR eluates at soil pH (determined by $CaCl_2$). The experiments were restricted to soil pH, because adsorption at pH values >11 was not expected.[22] For this purpose, 5 g of each soil was mixed with 25 mL of the respective eluate in 50-mL polypropylene centrifuge tubes. In order to obtain varying initial Cr^{VI} concentrations from the eluates, a dilution solution was prepared using the monsoon solution, Na_2CO_3 and NaCl. The dilution solution resembled the eluates in pH, alkalinity and electric conductivity. The eluates were diluted with the dilution solution to obtain Cr^{VI} concentrations ranging from 0.07 to 6.77 mmol L^{-1} for the Rania COPR eluate and 0.05 to 5.12 mmol L^{-1} for the Chhiwali COPR eluate, whereby the highest Cr^{VI} concentration complied with the undiluted eluate. The solutions were adjusted to soil pH using 0.1 M HCl. The samples were shaken for 24 h at room temperature in a horizontal shaker (3005, GFL Gesellschaft für Labortechnik) at 200 oscillations per minute and subsequently centrifuged and filtered through a 0.45-µm cellulose nitrate membrane filter. The Cr^{VI} concentration in the samples was measured as mentioned above. Under oxidising conditions and at pH >6.5, which was the case in this study, Cr^{VI} is normally the most stable oxidation state thermodynamically, so Cr^{VI} concentrations after equilibration are attributed to adsorption and not to reduction.

We evaluated the adsorption experiments by fitting the Freundlich (Eqn 2) and the Langmuir equations (Eqn 3) according to Essington[43] to the adsorption data using *Origin 8.5* (OriginLab: Friedrichsdorf, Germany):

$$a_{eq} = K_F \cdot c_{eq}^{\,n} \qquad [2]$$

$$a_{eq} = S_{max} \cdot K_L \cdot c_{eq} / (1 + K_L \cdot c_{eq}) \qquad [3]$$

where a_{eq} is the adsorbed amount of Cr (µmol kg^{-1}), K_F is the Freundlich constant (µmol^{1-n} kg^{-1} L^n), c_{eq} is the equilibrium concentration of Cr (µmol L^{-1}), n is the Freundlich exponent, S_{max} is a fitting parameter for the maximum amount of adsorbed CrO_4^{2-} (µmol kg^{-1}), and K_L is the Langmuir constant (L kg^{-1}).

3. Results

3.1 Physical and chemical properties of the soil samples

The samples were very slightly acidic to very slightly alkaline with pH values ranging from 6.7 to 7.2 (Table 1). Clay contents ranged from 10 to 190 g kg^{-1} and were dominated by illite in all samples. In addition the subsoil (#3) contained alternate layers of vermiculite and smectite as well as illite and smectite. The texture of the three soils was a silt loam according to Food and Agriculture Organization of the United Nations (FAO). Moreover, the samples had both low C_{org} contents (1.65 to 6.16 g kg^{-1}) and low C_{inorg} contents (0.73 to 1.40 g kg^{-1}, #2 was free of carbonates). Furthermore, the soil samples contained 5.07 to 8.15 g kg^{-1} of total pedogenic Fe (Fe_d), of which only 0.54 to 0.84 g kg^{-1} was short-range-ordered Fe (Fe_o). Hence the Fe_o-to-Fe_d ratio ranged from 0.07 to 0.17, indicating a larger proportion of crystallised Fe(hydr)oxides. Contents of Mn oxides were low and ranged from 0.15 to 0.31 g kg^{-1}. Total Fe contents ranged from 22.0 to 27.6 g kg^{-1}, indicating that most of the Fe is residually bound. Finally, total Cr contents ranged from 52.5 to 63.3 mg kg^{-1}, indicating that the soils were uncontaminated.

Table 1 Physical, mineralogical and chemical properties of the soils. The texture was determined according to the Food and Agriculture Organization of the United Nations (FAO). Vermiculite–smectite and illite–smectite were of alternating layers. Fe_o: contents of oxalate-extractable Fe, Fe_d: dithionite-citrate extractable Fe

Property		Rania Topsoil #1	Chhiwali Subsoil #2	Chhiwali Topsoil #3
Particle size distribution				
Sand	[g kg^{-1}]	220	250	240
Silt	[g kg^{-1}]	770	560	690
Clay	[g kg^{-1}]	10	190	70
Texture[A]	[–]	Silt loam	Silt loam	Silt loam
Smectite	[g kg^{-1}]	0.9	19.0	7.0
A.I.[B] vermiculite/smectite	[g kg^{-1}]	<0.01[C]	<0.01	7.7
Vermiculite/chlorite	[g kg^{-1}]	0.3	5.7	4.2
A.I. illite/smectite	[g kg^{-1}]	<0.01	<0.01	10.5
Illite	[g kg^{-1}]	8.7	163.4	39.9
Kaolinite	[g kg^{-1}]	0.1	1.9	0.7
pH (in H_2O)	[–]	8.0	8.0	8.6
pH (in $CaCl_2$)	[–]	6.9	6.7	7.2
Organic C	[g kg^{-1}]	6.16	1.65	5.02
Inorganic C	[g kg^{-1}]	1.40	<0.01	0.73
Total N	[g kg^{-1}]	0.68	0.26	0.65
C/N	[–]	11.1	6.3	8.8
Fe_o	[g kg^{-1}]	0.84	0.54	0.70
Fe_d	[g kg^{-1}]	5.07	8.15	6.06
Fe_o/Fe_d	[–]	0.17	0.07	0.12
Total Fe	[g kg^{-1}]	22.0	27.6	24.3
Total Mn	[g kg^{-1}]	0.26	0.38	0.30
Total Cr	[mg kg^{-1}]	52.5	54.9	63.3

[A] Below detection limit.

3.2 Chemical properties of the COPR eluates

Fig. 1 shows that dissolved Cr^{VI} increased at wider ratios and achieved a plateau at ratios between 1 : 5000 and 1 : 10 000. Whereas the Cr^{VI} content was 0.74 g kg^{-1} in the Rania sample and 0.58 g kg^{-1} in the Chhiwali sample at the 1 : 2 ratio, it increased to 16.4 g kg^{-1} (Rania) and 11.1 g kg^{-1} (Chhiwali) at the ratio of 1 : 10 000.

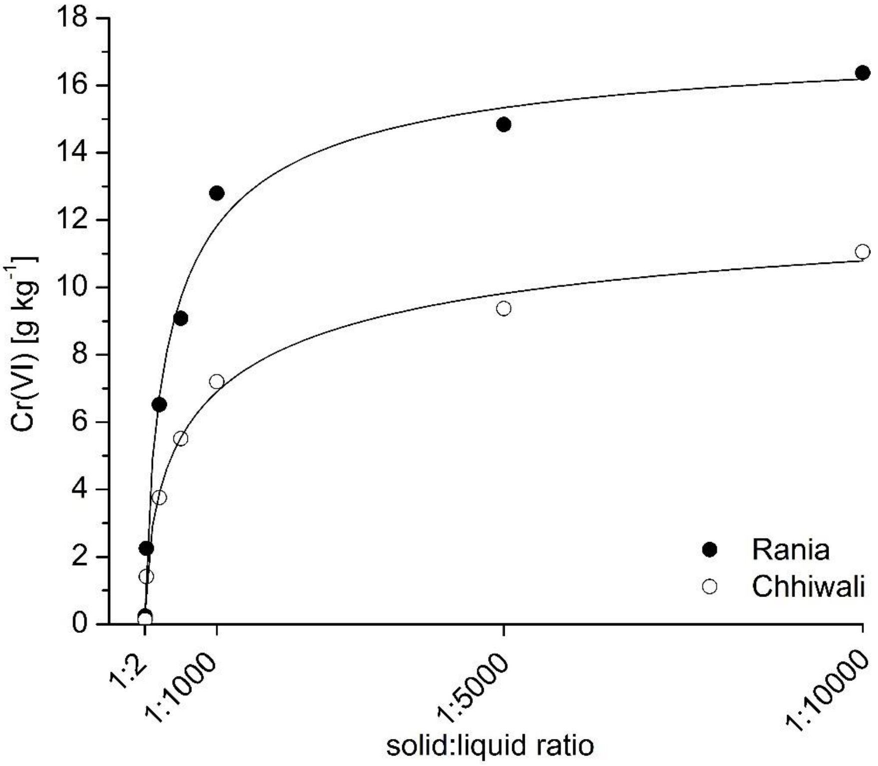

Fig. 1 Soluble chromium(VI) contents at different solid-to-liquid ratios in the chromite ore processing residue samples.

Table 2 displays the properties of the eluates at different solid-to-liquid ratios. The pH decreased from 12.3 to 8.5 (Rania) and 12.3 to 10.2 (Chhiwali) at the wider solid-to-liquid ratio and the alkalinity also decreased from 13.0 to 2.13 (Rania) and 14.1 to 1.91 (Chhiwali), with the largest changes occurring at the narrower solid-to-liquid ratios. However there was only a small decrease of the electric conductivity. Both COPR eluates at the solid-to-liquid ratio of 1 : 2 were very alkaline, with pH >12 (Table 3). There were no significant differences in electric conductivity (2.79 and 2.81 mS cm^{-1}) or alkalinity (13.9 and 14.1 mmol L^{-1}) between the eluates. However the Cr^{VI} concentration was 22 % higher for the Rania COPR eluate. There were also differences in the Ca and K concentrations, which were respectively 2.5 and 4 times higher in the Rania COPR eluate. In contrast, the Al, Na and Si concentrations were respectively ~3.5, 2 and 4 times higher in the Chhiwali COPR eluate. All other elements occurred only as traces in both eluates.

Table 2 Properties of the eluates at different solid-to-liquid ratios.

Sample	Solid-to-liquid ratio	pH [–]	Electric conductivity [mS cm^{-1}]	Alkalinity [mmol L^{-1}]	Dissolved Cr(VI) [g kg^{-1}]	Dissolved Cr(III) [g kg^{-1}]
Rania	1:2	12.3	2.79	13.9	0.74	0.03
	1:20	12.1	2.72	10.3	2.25	0.32
	1:200	11.7	2.63	4.29	6.52	1.02
	1:500	11.5	2.59	3.66	9.08	1.79
	1:1000	11.2	2.48	3.03	12.8	1.66
	1:5000	10.0	2.28	2.31	14.8	0.74
	1:10000	8.5	2.23	2.13	16.4	2.48
Chhiwali						
	1:2	12.3	2.81	14.1	0.58	0.02
	1:20	12.1	2.72	8.97	1.41	0.14
	1:200	11.5	2.64	3.67	3.76	0.46
	1:500	11.3	2.47	2.79	5.51	0.89
	1:1000	10.6	2.28	2.06	7.20	1.13
	1:5000	10.3	2.25	2.03	9.37	1.04
	1:10000	10.2	2.23	1.91	11.1	1.70

Table 3 Physical and chemical properties of the chromite ore processing residue eluates.

		Rania COPR	Chhiwali COPR
pH	[–]	12.3	12.3
Electric conductivity	[mS cm^{-1}]	2.79	2.81
Ionic strength	[mmol L^{-1}]	36.3	36.5
Alkalinity	[mmol L^{-1}]	13.9	14.1
Al	[mg L^{-1}]	1.92	6.56
Ca	[mg L^{-1}]	220	86.8
Cr(VI)	[mg L^{-1}]	372	290
K	[mg L^{-1}]	8.82	2.41
Na	[mg L^{-1}]	143	281
Si	[mg L^{-1}]	0.57	2.23
Sr	[mg L^{-1}]	0.49	0.24
As	[µg L^{-1}]	0.10	< 0.1[A]
Ba	[µg L^{-1}]	< 0.1	< 0.1
Cd	[µg L^{-1}]	< 0.1	< 0.1
Co	[µg L^{-1}]	3.60	3.90
Cu	[µg L^{-1}]	4.40	3.90
Fe	[µg L^{-1}]	14.9	6.50
Mg	[µg L^{-1}]	85.0	41.0
Mn	[µg L^{-1}]	5.00	1.10
Mo	[µg L^{-1}]	1.70	2.20
Ni	[µg L^{-1}]	2.70	5.80
Pb	[µg L^{-1}]	85.0	3.00
V	[µg L^{-1}]	3.30	18.8
Sb	[µg L^{-1}]	< 0.1	< 0.1
Se	[µg L^{-1}]	2.00	< 0.1
Zn	[µg L^{-1}]	64.7	88.8
F^-	[mg L^{-1}]	< 1	< 1
Cl^-	[mg L^{-1}]	9.36	4.42
SO_4^{2-}	[mg L^{-1}]	7.32	16.5
PO_4^{3-}	[mg L^{-1}]	< 1	< 1
NO_2^-	[mg L^{-1}]	< 1	< 1
NO_3^-	[mg L^{-1}]	< 1	< 1

[A] Below detection limit

3.3 Adsorption experiments

Figs 2 and 3 show the quantity of CrO_4^{2-} adsorbed by the three soils. Chromate adsorption was very low for both eluates and decreased in the order #2 > #1 > #3. Chromate adsorption was maximal for sample #2, which resulted from the lower pH and the higher content of pedogenic Fe oxides as the most significant adsorbents. There were no major differences in CrO_4^{2-} adsorption between the two COPR eluates. The only difference was in the solubility of CrO_4^{2-} from COPR and thus the initial CrO_4^{2-} concentration.

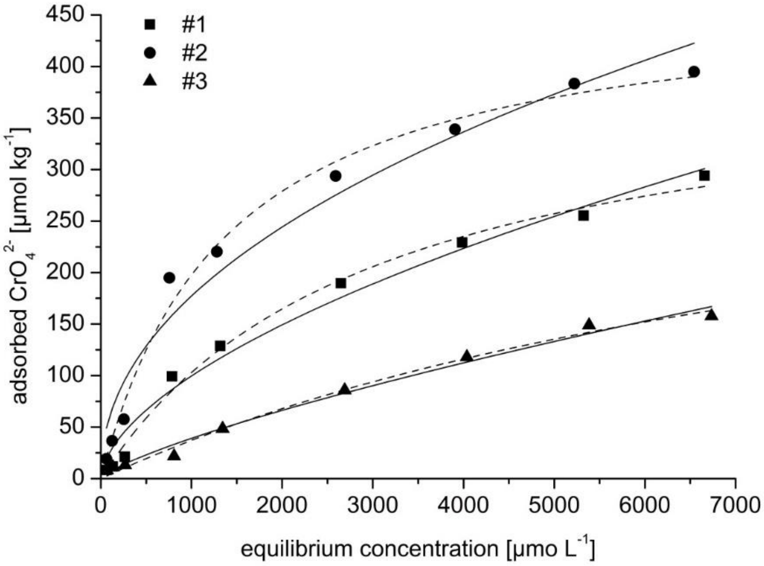

Fig. 2 Freundlich (solid line) and Langmuir (dashed line) adsorption isotherms of CrO_4^{2-} adsorption from Rania chromite ore processing residue eluate by three Indian soils.

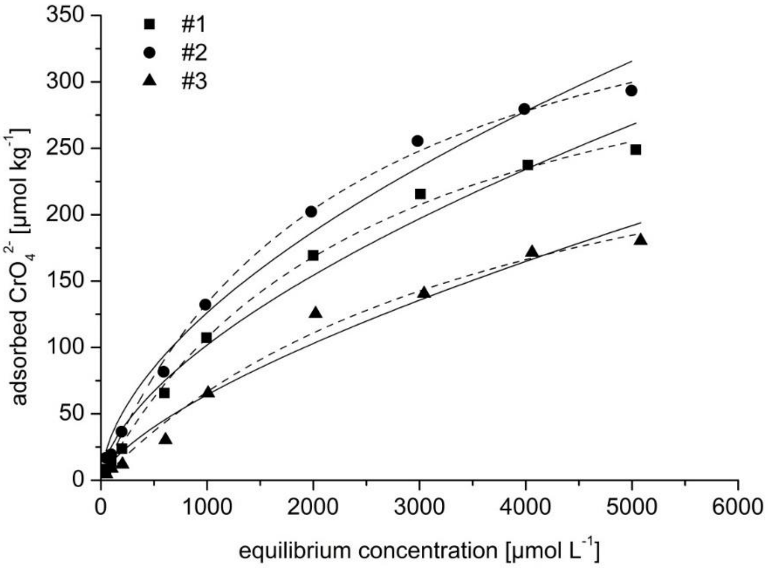

Fig. 3 Freundlich (solid line) and Langmuir (dashed line) adsorption isotherms of CrO_4^{2-} adsorption from Chhiwali chromite ore processing residue eluate by three Indian soils.

Table 4 displays the parameters and R^2 values of the Freundlich and Langmuir isotherms. Both the Freundlich and the Langmuir isotherms adequately reconstructed the adsorption data according to the coefficient of determination. However the coefficient of determination is slightly higher for the Langmuir isotherm (R^2 = 0.99) than for the Freundlich isotherm (R^2 = 0.96 to 0.99). The empirical Freundlich equation is based on adsorption onto a heterogeneous surface.[43] Moreover the Freundlich isotherm is valid only for adsorption occurring at low solution concentration.[44] In the case of higher CrO_4^{2-} concentration, the Freundlich equation no longer represents adsorption, as the adsorption sites become saturated and the isotherms reach a plateau. To explain CrO_4^{2-} adsorption at higher concentrations and to describe an adsorption maximum, Langmuir isotherms were used. According to Essington[43] the Langmuir model is valid for monolayer adsorption on surfaces with a finite number of similar active sites (homogeneous surface). The isotherms for the CrO_4^{2-} adsorption increased with higher slope in the initial stage at low values of a_{eq} and c_{eq}, which indicates that numerous readily accessible sites were initially available (Figs 2, 3). At higher c_{eq} values, a plateau was reached, which confirms the monolayer coverage of CrO_4^{2-} on the surfaces.

Table 4 Parameters and R^2 values of the Freundlich and Langmuir isotherms for the three soils. K_F is the Freundlich constant, c_{eq} is the equilibrium concentration of Cr, n is the Freundlich exponent, S_{max} is a fitting parameter for the maximum amount of adsorbed CrO_4^{2-}, and K_L is the Langmuir constant

		Freundlich			Langmuir		
		K_F [μmol^{1-n} kg^{-1} L^n]	n	R^2	S_{max} [μmol kg^{-1}]	K_L [L kg^{-1}]	R^2
#1	Eluate Rania	1.77	0.58	0.979	411	$3.34\cdot10^{-4}$	0.993
#2		7.25	0.46	0.959	473	$7.18\cdot10^{-4}$	0.990
#3		0.20	0.76	0.987	400	$1.02\cdot10^{-4}$	0.991
#1	Eluate Chhiwali	1.60	0.60	0.978	389	$3.81\cdot10^{-4}$	0.998
#2		2.46	0.57	0.981	436	$4.41\cdot10^{-4}$	0.997
#3		0.59	0.68	0.971	332	$2.51\cdot10^{-4}$	0.988

The K_F values (Table 4) reflected the reciprocal relation of pH and adsorption and were highest for the soil with the lowest pH. Thereby the affinity for CrO_4^{2-} adsorption in the Rania COPR eluate was slightly higher for #2 compared to CrO_4^{2-} adsorption from the Chhiwali COPR eluate by #2. However for samples #1 and #3 it was the other way around, because altogether the CrO_4^{2-} adsorption affinity was approximately similar for these two eluates. The adsorption maxima predicted from each isotherm ranged from 400 (#3) to 473 (#2) mmol kg^{-1} for the Rania COPR eluate and 332 (#3) to 436 (#2) mmol kg^{-1} for the Chhiwali eluate, which shows that only small amounts of CrO_4^{2-} could be adsorbed by the investigated soils.

4. Discussion

The results showed a dependence of CrO_4^{2-} adsorption on pH, which decreased with increasing pH. The pH of the soils controls the adsorption capacity because of its influence on the functional groups of the adsorbent as well as the species distribution of the adsorbate. An increase in pH causes a decrease of the positive surface charge and an increase of the negative surface charge in soils. A negative surface charge does not favour the adsorption of CrO_4^{2-} and, as a consequence, repulsion of CrO_4^{2-} from the soil surface is expected. These findings have also been reported by other investigators.[27,29,45] It should be noted that CrO_4^{2-} adsorption also occurs to some extent at neutral and slightly alkaline pH, as a result of non-electrostatic adsorption. Thereby ligand exchange reactions between CrO_4^{2-} and hydroxy ligands of the adsorbent occur and inner-sphere surface complexes are formed.[29] Ferreiro et al.[46] reported that, for molybdate, ligand exchange reactions occur predominantly between species of similar charge, and therefore between the anion and –OH but not for the protonated groups $(–OH)^+$ or $(–OH_2)^+$. We thus assume a similar effect for CrO_4^{2-}.

A further factor that may influence CrO_4^{2-} adsorption is the ionic strength, which is exceptionally high in the COPR eluates compared with natural soil solutions. Experiments of Mesuere and Fish[47] showed that an ionic strength of 50 mmol L^{-1}, which is in the range of our experiment, slightly reduces the CrO_4^{2-} adsorption, although the effect was more distinct at an ionic strength of 500 mmol L^{-1}. In contrast, Ajouyed et al.[27] did not observe ionic strength to have an effect on CrO_4^{2-} adsorption on hematite and goethite up to an ionic strength of 100 mmol L^{-1}. However, CrO_4^{2-} adsorption on α-alumina was distinctly already reduced at an ionic strength of 10 mmol L^{-1}. The ionic strength can influence the double layer thickness and interface potential, which affect the binding of the adsorbate on the surface sites.[27] Thereby outer-sphere surface complex formation is more influenced by the ionic strength than inner-sphere surface complex formation since the ions are placed in the same plane for outer-sphere surface complexes.[27] Regarding the influence of the ionic strength on the formation of inner-sphere surface complexes, Jiang et al.[28] found that with increasing ionic strength the surface charge of the soil particles becomes more negative when the pH is higher than the point of zero salt effect (pH_{PZSE}). Thereby the number of cations in the adsorption plane increase with increasing ionic strength, however, that makes the potential at the adsorption plane less negative, which enhances CrO_4^{2-} adsorption.[28] If the pH is lower than pH_{PZSE}, the soil surface charge increases with increasing ionic strength. However, an increase of anions in the adsorption plane with increasing ionic strength can cause the reduction of the potential at the adsorption plane, which results in lower CrO_4^{2-} adsorption.[28,47] The latter case may be important, since we assume that Fe oxides are the predominant adsorbents in the investigated soils, which normally have a pH_{PZSE} >8.[43] Furthermore, anions such as SO_4^{2-} and CO_3^{2-} compete for binding sites and reduce the positive surface charge, which results in a decrease of the electrostatic attraction for negatively charged ions, including CrO_4^{2-}.[18] Indeed, the SO_4^{2-} concentration in the COPR eluates is 50-fold (Rania) and 18-fold (Chhiwali) lower than the CrO_4^{2-} concentration, so this aspect is circumstantial. Overall, it is likely that the effect of ionic strength itself on CrO_4^{2-} adsorption is only intermediate; instead it is important which ions dominate in the solution.

Moreover, the high concentration of carbonate in the COPR eluates may also negatively affect CrO_4^{2-} adsorption. Villalobos et al.[34] and van Geen et al.[48] reported that CrO_4^{2-} adsorption was significantly reduced in the presence of carbonate due to competition for surface sites and surface electrostatic repulsion. Furthermore, Villalobos et al.[34] showed that CrO_4^{2-} adsorption switches from inner-sphere to outer-sphere surface complexes with increasing carbonate concentration. This may be important, considering that the bindings in outer-sphere surface complexes are not as strong as those in inner-sphere surface complexes and CrO_4^{2-} might be desorbed. Furthermore, other anions can compete for electrostatic binding sites. Zachara et al.[18] also reported that CrO_4^{2-} adsorption on amorphous Fe oxyhydroxides was highly influenced by aqueous carbonate species.

A major difference between the COPR eluates was the initial Cr^{VI} concentration. Both COPR eluate concentrations exceeded the WHO guideline value for Cr, which is set as 50 µg L^{-1}, by more than 1000-fold at the 1 : 2 solid-to-liquid ratio. It should be noted that the WHO does not differentiate between Cr^{III} and Cr^{VI}, although Cr^{VI} is much more toxic. The concentrations of Cr^{VI} in the COPR eluates are typical for most of the COPRs. Foeldi et al.[11] investigated the properties of six COPRs obtained from the area of Kanpur at different solid-to-liquid ratios and found Cr^{VI} concentrations ranging from 55 to 355 mg L^{-1} at a 1 : 2 solid-to-liquid ratio. The Cr^{VI} concentrations exceeded the calibration limit in three samples, but the Cr concentration, which approximately equalled the Cr^{VI} concentration, ranged from 615 to 7650 mg L^{-1}, indicating that some COPR leached much more Cr^{VI}. The process that may be responsible for the release of Cr^{VI} is the dissolution of Cr^{VI}-hosting mineral phases.[15] Geelhoed et al.[15] investigated the processes controlling leaching of Cr^{VI} from COPR and concluded that Cr^{VI}-hydrogarnet and Cr^{VI}-hydrocalumite control the solubility of Cr^{VI} at pH values above 11.

On comparing CrO_4^{2-} adsorption from COPR eluates with that from synthetic Cr^{VI} standard solutions as presented in the literature, we could only observe partial differences. However, a direct comparison of adsorption affinity and adsorption capacity reported in the literature is difficult because of varying experimental conditions. Use of these models to predict adsorption under changing conditions of solution concentration, ionic strength and pH is not possible.[49] Our K_F values were in the range of the results of the adsorption experiments performed by Choppala et al.[45] They were carried out with a potassium dichromate standard solution and 12 Australian soils with different properties, of which four soils were of relevance to our study because of their neutral or alkaline pH ranging from 6.5 to 8.0. The four considered soils also showed low CrO_4^{2-} adsorption. Surprisingly, Choppala et al.[45] found that CrO_4^{2-} adsorption was correlated with positive charge and with Fe oxides but not with pH. This might arise from the fact that without significant amounts of adsorbents with functional groups, a low pH cannot increase adsorption. The adsorption capacities derived from our adsorption experiments are somewhat lower compared to those obtained from the experiments by Choppala et al.[45] A possible reason is the higher content of Fe oxides in the Australian soils, which ranged from 9.8 to 20.6 g kg^{-1} (one sample had only 0.1 g kg^{-1} of Fe oxides but a high clay and organic matter content). In contrast, it is possible that the high ionic strength and content of carbonates in the COPR eluates reduces the adsorption capacity up to 24-fold.

This study showed that CrO_4^{2-} adsorption from COPR eluates was similar to those from experiments with Cr^{VI} standard solutions, which can be used as analogues. The same factors affect CrO_4^{2-} adsorption, whereby a high soil pH and low content of Fe-oxides are the main factors that control CrO_4^{2-} adsorption. Hence in all investigated Indian soils, CrO_4^{2-} adsorption was found to be very low. It is likely that the chemical composition of the COPR eluate decreased CrO_4^{2-} adsorption because of its high pH, ionic strength and the dissolved carbonate as a competitive anion. Considering the amounts of CrO_4^{2-} leached from the COPR, the extent of adsorption and the chemical composition of the COPR eluates, we expect a high discharge of CrO_4^{2-} from the COPR into the groundwater. Especially during the three-month monsoon period, groundwater contamination in areas surrounding the disposal sites will occur. In this context remediation strategies as well as groundwater monitoring are needed.

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Chapter 6 Chromium release from a COPR-contaminated soil at varying water content and redox conditions

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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.

Abbreviations:

E_H, redox potential; COPR, chromite ore processing residue; BSC, basic chromium sulfate; OM, organic matter

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_H). In this study, the influence of E_H 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_H dropped slowly to minimum values of around –100 mV (calculated to pH 7), while E_H was controlled by $CrO_4^{2-}/Cr_2O_3(s)$, or $CrO_4^{2-}/(Fe,Cr)OOH$ redox couples. Soil drainage resulted in a quick return to oxidizing conditions; i.e., $E_H > 300$ mV. The Cr species distribution and release showed a clear trend with E_H. At the beginning of the experiment, under oxidizing and weakly reducing conditions (E_H range from >100 to 300 mV), Cr(VI) was released in particular. However, under moderately reducing conditions (E_H 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.

Keywords

Chromium, speciation, redox potential, water regime, India, soil

1. Introduction

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 (Ansari et al., 1999; Sinha et al., 2006; Srinivasa Gowd et al., 2007; Singh et al., 2009; Srinivasa 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-lime 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 chromite 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 $\geq$6.7 depending on pK_a and concentrations of complexing ligands (James and Bartlett, 1983).

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) up 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 E_H–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 results 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.

2. Material and methods

2.1 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 Chhiwali, 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).

2.2 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_2O_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_o) 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_2CO_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 USEPA (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). Otherwise it was measured as described before.

2.3 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, the 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 Mansfeldt (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

$$E_H\ (\text{pH } 7) = E_H + (\text{pH} - 7) \cdot 59. \qquad [1]$$

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 given oxidation–reduction reaction in which

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

However, the value of 59 mV per pH unit is probably as good a conversion factor as any, and adjustment makes comparison between different media definitively 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, Vacubrand, Wertheim, Germany). According to the Van Genuchten equation (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 Stone Daemon DL. (Schaap et al., 2001), and implemented soil data of percentage particle size fraction and bulk density.

Table 1 Sequence of experimental steps and calculated pressure heats.

Step	Adjusted matrix potential hPa	Duration d	Cumulative time d
Upstream infiltration	–	0.25	0.25
Saturation	0	61.92	62.17
Suction	–10	7.78	69.95
	–40	7.01	76.96
	–60	6.94	83.90
	–100	7.23	91.13
Upstream infiltration	–	0.16	91.29
Saturation	0	28.08	125

During water saturation, and each matrix potential step, 6 mL pore water from each suction cup was sampled periodically (every 2-7 days). 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 (Unitrode, Metrohm, Filderstadt, Germany). 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}, they 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).

2.4 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.

3. Results

3.1 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 3.36 g kg^{-1} of total pedogenic Fe (Fe_d), of which 1.06 g kg^{-1} was short-range-ordered Fe (Fe_o). Hence the Feo:Fed 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.

Table 2 Physical and chemical properties of the soil.

Property		
Particle size distribution		
Sand	g kg^{-1}	110
Silt	g kg^{-1}	750
Clay	g kg^{-1}	140
Texture†		Silty loam
pH (in $CaCl_2$)	—	8.4
pH (in H_2O)	—	10.3
Organic C	g kg^{-1}	4.87
Inorganic C	g kg^{-1}	5.72
Total N	g kg^{-1}	0.50
C/N	—	21.2
Fe_o	g kg^{-1}	1.06
Fe_d	g kg^{-1}	3.36
Fe_o/Fe_d	—	0.32
Total Fe	g kg^{-1}	25.0
Total Mn	g kg^{-1}	0.41
Total Cr	g kg^{-1}	0.544
Cr(VI)	g kg^{-1}	0.036

†According to FAO

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.

3.2 Redox potential and pH in pore water

Figure 1a and 1b 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 afterwards 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). Resaturation caused the E_H to decrease again, but the decrease was distinctly faster than during the first saturation period. Thus, the E_H complied 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 column section, 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.

3.3 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 of Mn concentration 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 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.

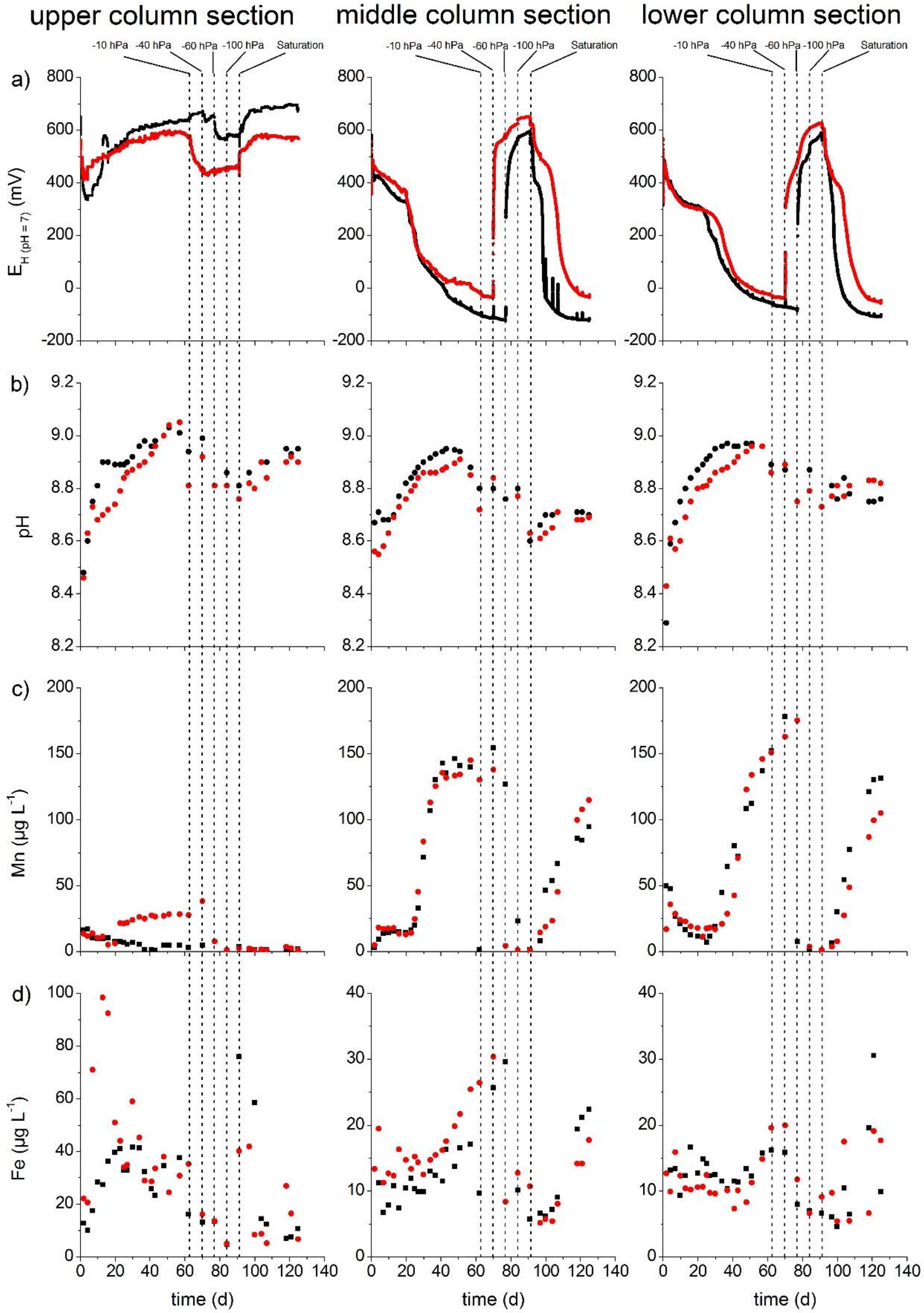

Fig. 1 Development of redox potential (E_H), pH, Mn and Fe concentrations during the column experiment (black point = column A, red point = column B). Dashed lines indicate matrix potential changes.

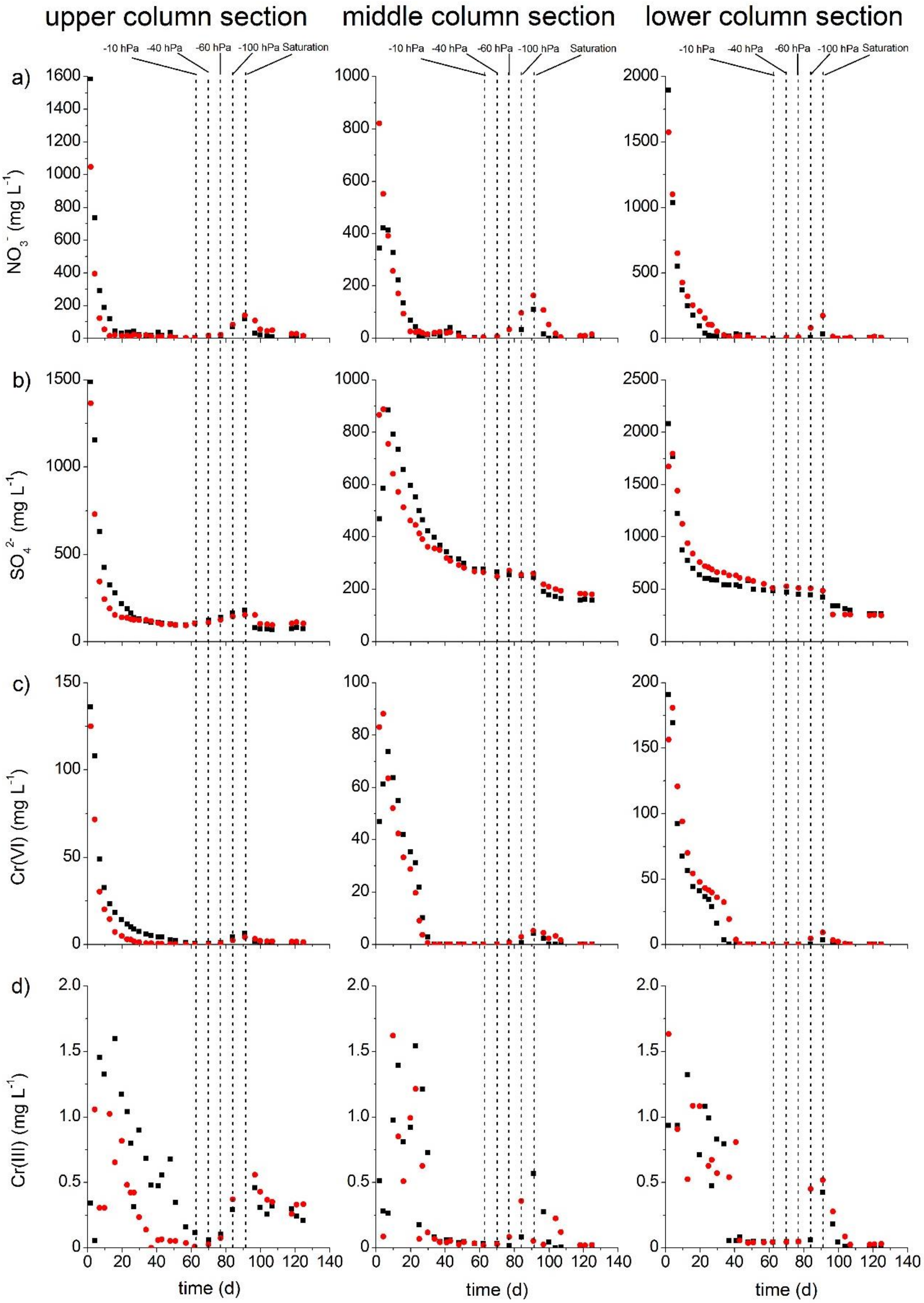

Fig. 2 Development of NO$_3^-$, SO$_4^-$, Cr(VI), and Cr(III) concentrations during the column experiment (black point = column A, red point = column B). Dashed lines indicate matrix potential changes.

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.

3.4 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 section. 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 $K_{1/2}$. 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 decreased again up to around 1 mg L^{-1} in the upper section, and <20 µg L^{-1} in the middle and lower sections.

Chromium(III) concentrations decreased from around 1.6 mg L^{-1} to < 1 mg L^{-1} after 25 d, and <50 µg L^{-1} after 70 d, whereby 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.

4. Discussion

4.1 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 NO_3^- was reduced to N_2O, N_2, or 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 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 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 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 $CrO_4^{2-}/Cr_2O_3(s)$, or CrO_4^{2-}/(Fe,Cr)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.

4.2 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 $Cr(OH)^{2+}$ hydrolysis 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 (Hooda, 2010; Rai et al., 1987). 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; Zhilin 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 (Zhilin 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 be observed by Couture et al. (2015). However, Hindersmann 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 a 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 E_H 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 E_H. 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.

4.3 Within-column differences of E_H and Cr mobilization

There were no significant differences in the course of soil E_H between the middle and lower column sections. However, the E_H 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 E_H. 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, NO_3^-, SO_4^{2-}, 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 NO_3^- 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 E_H is probably in the upper range of moderately reducing conditions.

4.4 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 E_H 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 NO_3^- and SO_4^{2-} 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 redox 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).

5. 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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Supplementary material

Chromium release from a COPR-contaminated soil at varying water content and redox conditions

Table S1 Redox reactions and their theoretical equilibrium redox potential (E^0, in V relative to the standard hydrogen electrode) for dominant redox species at standard state and at pH = 7 (according to Reddy and DeLaune, 2008).

Reaction	E^0 (V) pH = 0	E^0 (V) pH = 7
$O_2 + 4H^+ + 4\ e^- \rightleftharpoons 2H_2O^\dagger$	1.23	0.81
$2\ NO_3^- + 12\ H^+ + 10\ e^- \rightleftharpoons N_2 + 6H_2O$	1.24	0.82
$MnO_{2(s)} + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	1.29	0.87
$CrO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O^\dagger$	1.51	0.41
$Fe(OH)_{3(s)} + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3\ H_2O$	0.80	0.38
$SO_4^{2-} + 10H^+ + 8e^- \rightleftharpoons H_2S + 4\ H_2O$	0.34	-0.08

† according to Brezonik and Arnold (2011)

Table S2 Sequential extraction of Cr in the contaminated agriculture soil.

Fraction	mg kg^{-1}	%
F1†	24.6	4.54
F2	22.8	4.20
F3	6.73	1.24
F4	6.89	1.27
F5	233	42.9
F6	147	27.1
F7	102	18.7
Sum ‡	542	100
Total Cr §	544	
Sum/Total Cr	0.99	

† Fraction (F1): mobile, F2: exchangeable, F3: Mn oxide, F4: organic, F5: short-range-ordered Fe (hydr)oxides, F6: crystalline Fe (hydr)oxides, and F7: residual pool

‡ Sum F1–F7

§ Separate aqua regia digestion

Table S3 Reduction rate of Cr(VI) in soil column experiment.

section	Rate constant (s^{-1})	Correlation coefficient
upper column section A	5.4	0.98
middle column section A	17.4	0.96
lower column section A	9.2	0.96
upper column section B	3.9	0.99
middle column section B	12.6	0.98
lower column section B	11.3	0.95

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Fig. S1 Sampling site in Godhrauli, Uttar Pradesh, North India.

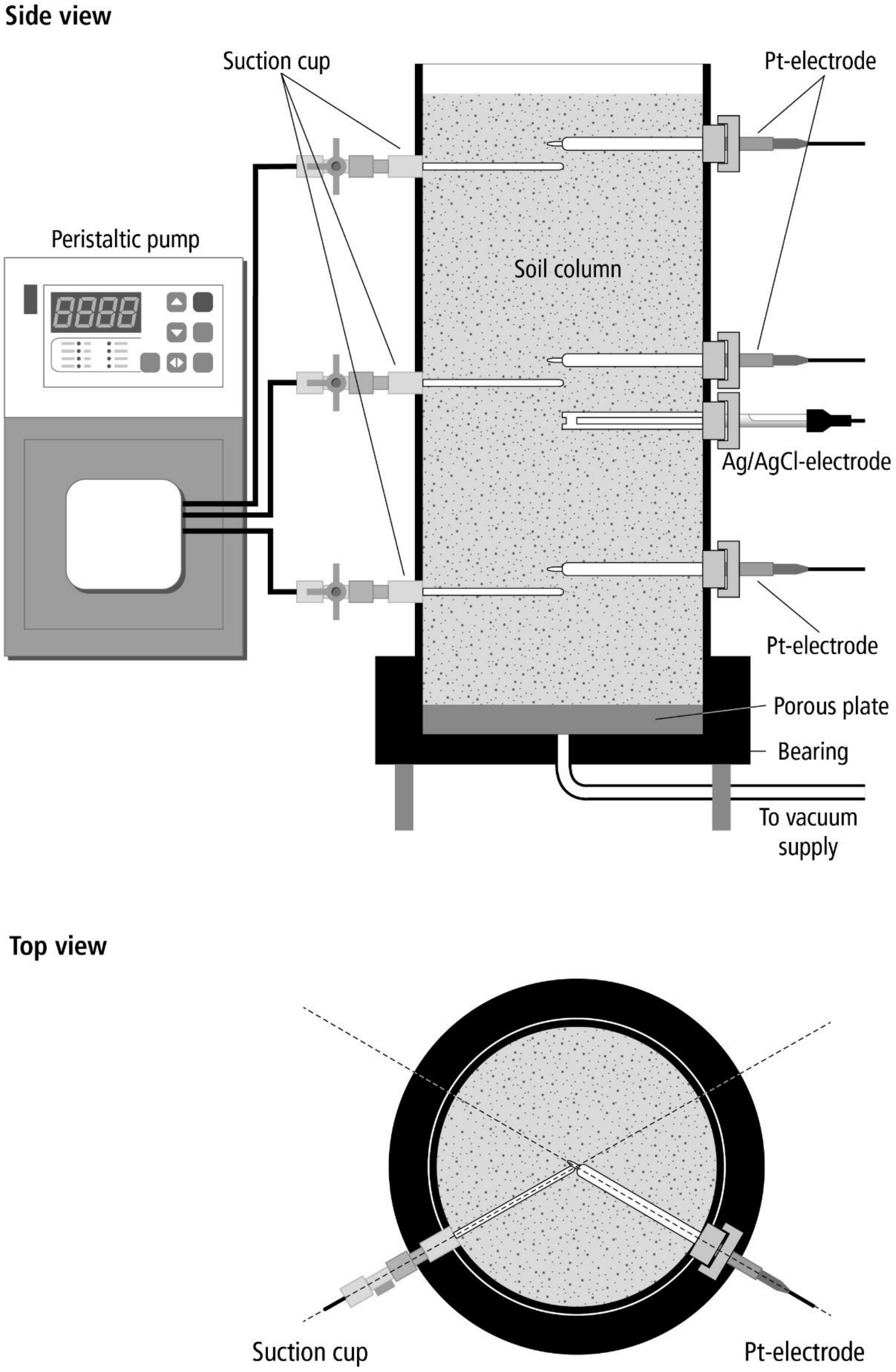

Fig. S2 Scheme of the experimental setup (modified from Weigand et al., 2010).

Chapter 7 Environmental status of groundwater affected by chromite ore processing residue (COPR) dumpsites during pre-monsoon and monsoon seasons

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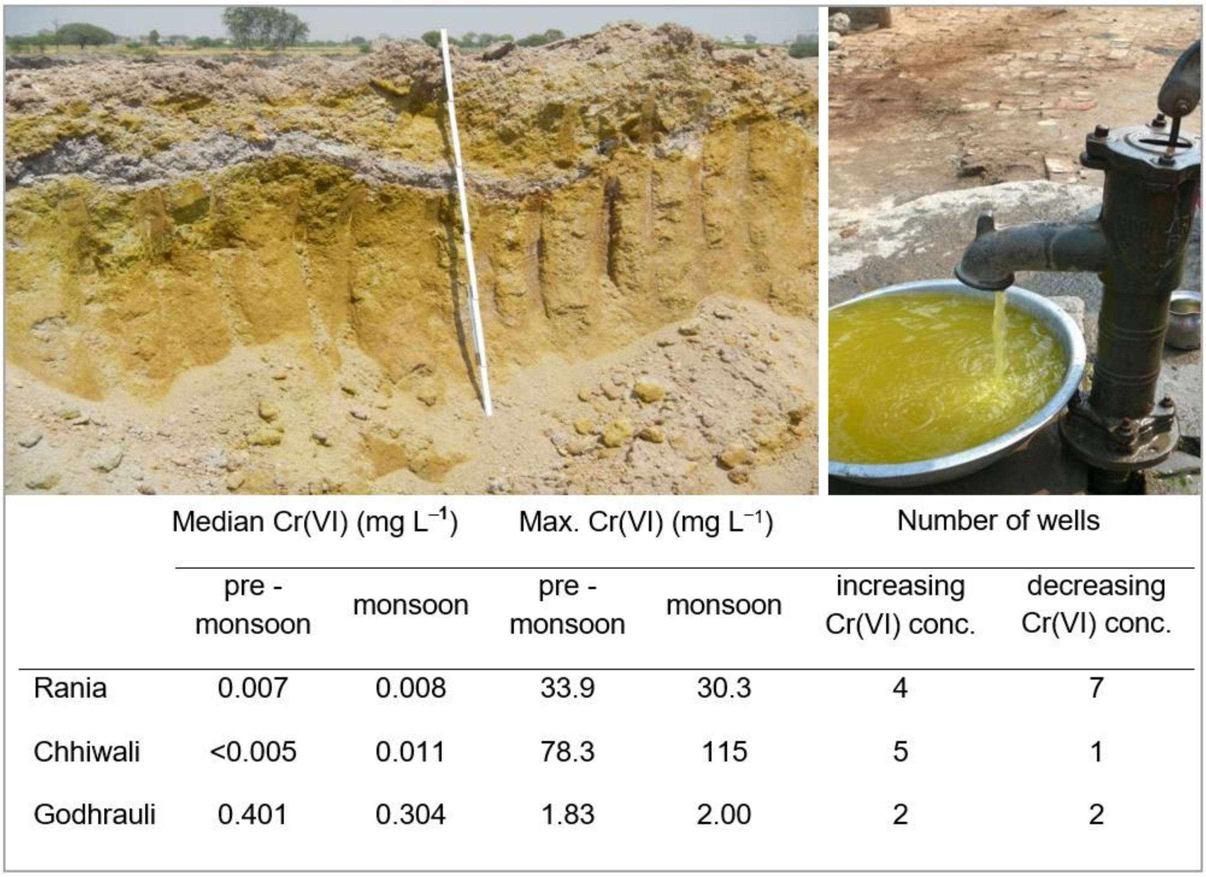
Graphical abstract



	Median Cr(VI) (mg L^{-1})		Max. Cr(VI) (mg L^{-1})		Number of wells	
	pre - monsoon	monsoon	pre - monsoon	monsoon	increasing Cr(VI) conc.	decreasing Cr(VI) conc.
Rania	0.007	0.008	33.9	30.3	4	7
Chhiwali	<0.005	0.011	78.3	115	5	1
Godhrauli	0.401	0.304	1.83	2.00	2	2

Abstract

Chromite Ore Processing Residue (COPR) is generated by the roasting of chromite ores for the extraction of chromium. Leaching of carcinogenic hexavalent chromium (Cr(VI)) from COPR dumpsites and contamination of groundwater is a key environmental risk. The objective of the study was to evaluate Cr(VI) contamination in groundwater in the vicinity of three COPR disposal sites in Uttar Pradesh, India, in the pre-monsoon and monsoon seasons. Groundwater samples ($n = 57$ pre-monsoon, $n = 70$ monsoon) were taken in 2014 and analyzed for Cr(VI) and relevant hydrochemical parameters. The site-specific ranges of Cr(VI) concentrations in groundwater were <0.005 to 34.8 mg L^{-1} (Rania), <0.005 to 115 mg L^{-1} (Chhiwali), and <0.005 to 2.0 mg L^{-1} (Godhrauli). Maximum levels of Cr(VI) were found close to the COPR dumpsites and significantly exceeded safe drinking water limits (0.05 mg L^{-1}). No significant dependence of Cr(VI) concentration on monsoons was observed.

Keywords

chromium; speciation; chromite ore processing residue; monsoon hydrology; groundwater, India

1. Introduction

Chromium (Cr) is a widely used element in various industrial activities such as metal plating, leather tanning, etc. (Kimbrough et al. 1999). It is a redox-sensitive transition metal and exists in the environment in either the trivalent (Cr(III)), or hexavalent (Cr(VI)) oxidation states. Its chemical properties and environmental behavior are directly related to the dominant valence state. While Cr(III) is considered to be essential to mammals for the maintenance of normal carbohydrate, lipid and protein metabolism (Pechova and Pavlata 2007), Cr(VI) is known to be carcinogenic when inhaled (Holmes et al. 2008) or ingested, e.g. with drinking water (Sun et al. 2015). However, the most widely known reaction of Cr(VI) is sensitization and elicitation of allergic contact dermatitis (Shelnutt et al. 2007). Furthermore, Cr(VI) compounds are also highly toxic to plants and are detrimental to their growth and development (Nagajyoti et al. 2010). Due to its toxicity, the World Health Organization determined a guideline value of 0.05 mg L^{-1} for total Cr in drinking water (WHO 2011).

Extensive groundwater contamination with Cr has been reported in the area of Kanpur (Uttar Pradesh, North India), which hosts a prominent cluster of leather-processing industries. The geochemical behavior and distribution of Cr in aquifers have been studied in industrial areas of Kanpur (Ansari et al. 1999, 2000; Dwivedi et al. 2015; Singh et al. 2009; Srinivasa Gowd et al. 2010), Unnao (Dwivedi et al. 2015; Srinivasa Gowd et al. 2010; Srivastava and Singh 2014) and Rania (Prakash et al. 2011; Singh et al. 2013). Apart from groundwater contamination caused by industrial effluents, the illegal disposal of Cr-containing waste is a primary Cr source. This waste originates from production sites of basic chromium sulfate (BCS) located in Rania, and in Chhiwali, 30 and 40 km away from Kanpur, respectively. Production of BCS occurs via the high-lime process through which the insoluble Cr(III) present in the ore is converted to soluble Cr(VI) and extracted by aqueous leaching (Burke et al. 1991). The waste of this process is the so-called chromite ore processing residue (COPR), which is dumped at uncontrolled landfills close to the factories or in adjacent villages. Besides the large landfills, COPR is found elsewhere in these areas, because it is commonly used in road construction, in berms, and as foundation and backfill. Residual Cr contents of 81 and 74 g kg^{-1} have been measured in the COPR at two manufacturing sites, of which 20% and 13%, respectively, were present as Cr(VI) (Matern et al. 2016). Deposited COPR is not stable and undergoes weathering, resulting in destabilization and dissolution of Cr(VI)-bearing minerals (Chrysochoou et al. 2010; Geelhoed et al. 2002; Geelhoed et al. 2001). Leaching of Cr(VI) from COPR was evident from the strong yellow stain of well water. Field test-kits indicated Cr(VI) concentrations of up to 80 mg L^{-1} in piezometers close to the main dumpsite in Rania (Singh et al. 2013). Leaching of Cr(VI) from the COPR waste is directly linked to the incidence of seepage water, expected to occur mainly during the monsoon season (July-September). It was, therefore, hypothesised that Cr(VI) influx to the underlying aquifers would vary seasonally.

Chromium(VI) contamination of groundwater affected by COPR is not only an Indian issue but a key environmental risk arising at COPR sites worldwide. Concentrations up to 91 and 6.7 mg L^{-1} Cr(VI) have been measured in Scottish COPR-affected groundwater and tributary stream, respectively (Farmer et al. 2002). Burke et al. (1991) detected Cr(VI) concentrations up to 30 mg L^{-1} in groundwater samples in New Jersey COPR-affected areas. Groundwater contamination has been also reported for China, Baltimore (Maryland), and Japan (Burke et al. 1991; Li et al. 2011; Sun et al. 2014).

The objectives of this study were (i) to identify and map the COPR waste sites in three industrial areas, (ii) to investigate the geochemical characteristics of groundwater in the surroundings of the COPR sites, (iii) to asses and classify the groundwater quality with respect to Cr(VI) contamination, and (iv) to elucidate the influence of monsoonal precipitation on Cr(VI) mobilization from COPR sites. The findings of this study describe the spatial dimension of Cr(VI) contamination for three CORR-contaminated sites, which is fundamental for the evaluation of environmental risks and remediation strategies. This is important, since the local population uses the groundwater not only for livestock rearing and irrigation but also for drinking.

2. Material and methods

2.1. Study area

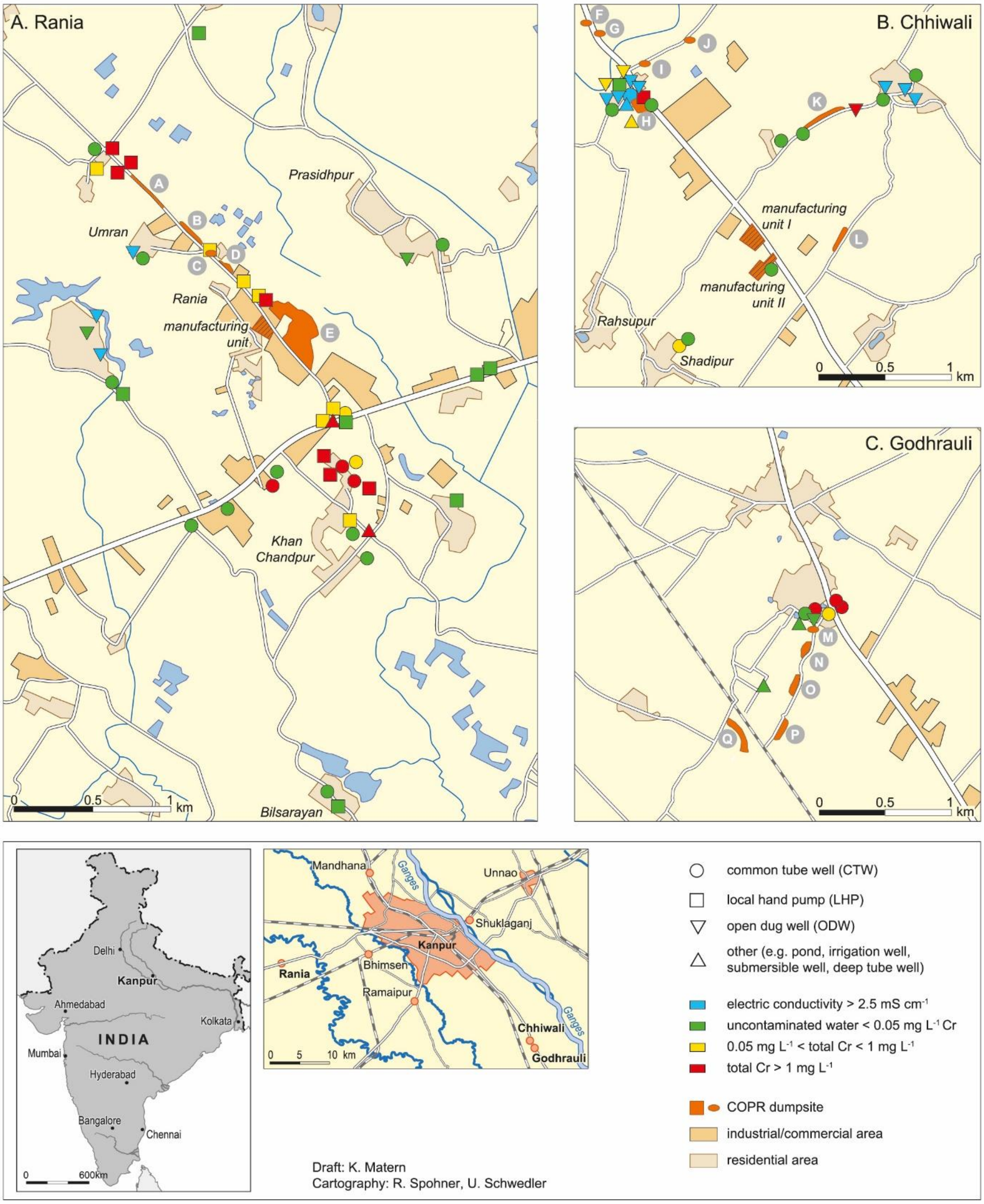
The present study was carried out in the villages of Rania, 30 km to the west of Kanpur (district Kanpur Dehat) as well as in Chhiwali and Godhrauli, 40 and 47 km, respectively, to the southeast of Kanpur (district Fatehpur), in the State of Uttar Pradesh, North India (Fig. 1). These areas contain sites of historic or current production of the BCS used in the leather tanning process. In Rania, the production of BCS commenced in the late 1980s with the first manufacturing unit. In 1992, four manufacturing units were already operating. These works were closed in 2005 due to raised environmental concerns. However, COPR from the production of BCS has been disposed of in surrounding fields. In Chhiwali, two Cr works were established in 2004, which are still in operation. Several illegal waste dumps of unknown area and thickness were found near Chhiwali and its neighboring village, Godhrauli.

2.2. Geology and climate

Geologically the study area is located in the central alluvial Ganga plain that was formed in response to the development of the Himalayas (Rao 1973; Singh 1996), and remains an important link between Himalayan Orogen and Indian Ocean since the early Quaternary period until now (Sinha et al. 2010). The modern landscape of the region was primarily formed due to the late Glacial/ early Holocene incisions associated with an intensified monsoon. The area has an almost flat topography gently running from northwest to southeast (Singh et al. 2006b). These regions have a distinct stratigraphy. As opposed to earlier belief that contribution of sediments responsible for these plains has been predominantly from Himalayas during most of the Quaternary period, recent findings suggest that a contribution of sediments from cratonic sources was also significant during the late Quaternary period (Sinha et al. 2010). Such competition between Himalayan and cratonic sources of sediments is evident in the subsurface alluvial stratigraphy in the region. The alluvial deposits of the Ganga plains are predominantly constituted of micaceous sand, silt, clay, gravel, and kankar; the maximum thickness of alluvium being ~500 m above bedrock of Bundelkhand granite (Srivastava et al. 2013). In Nauraiya Khera (Kanpur), which is ~30 km east of the present study area, wells were constructed to provide information about the subsurface lithology of the region up to a depth of 50 m bgl using piezometers. These investigations indicated that sediments in the area consist of distinct layers of clay, fine sand, clay, medium sand, clay and kankar, fine sand, and clay and kankar with varying thicknesses (Singh et al. 2009). These authors also developed fence plots of the subsurface lithology which indicated the wedge shaped and non-uniform nature of sandy clay as well as sand layers.

In the study area, a three-tier aquifer system exists. A shallow (upper) aquifer including the phreatic zone extends to varying depths of 25 to 130 m, a middle aquifer is located between 90 and 240 m, and a lower aquifer extends to depth between 180 and 450 m (Singh et al. 2006a). The upper aquifer forms the main source of water supply to the dug wells and shallow tube wells (Singh et al. 2006a), and has been observed to be most contaminated with hexavalent chromium (Singh et al. 2009).

The study area is situated in the humid subtropical climate zone characterized with cool (November-February), hot (April-June) and monsoon (July-September) seasons. Heavy rainfall typically occurs during the monsoon season in July, August and September, accounting for almost 70 to 80% of the total precipitation (Chowdhury et al. 1982). Since the monsoonal rain normally arrives in this area as early as June, two periods are determined for the convenience of description, namely pre-monsoon period (March-May), a time before the occurrence of monsoonal rain and monsoon period (June-September). From 2009 to 2013, the average rainfall was 689 mm in the Kanpur Dehat district and 681 mm in the Fatehpur district (India Meteorological Department (IMD 2015a), with about 85% and 89%, respectively, taking place during monsoon (IMD 2015a).



Draft: K. Matern
Cartography: R. Spohner, U. Schwedler

Fig. 1 Location of the area with COPR dumpsites and the investigated wells.

2.3. Sampling

Altogether 75 wells were investigated, from which 57 groundwater samples were collected in the pre-monsoon period in April 2014 and 70 samples at the end of the monsoon period in September 2014. The intention was to sample identical wells in the two sampling campaigns.

However, some wells were not available during the second sampling campaign. In this case, alternative wells, close to the original ones, were chosen. Overall, samples were taken from 52 wells in both seasons. Groundwater samples were collected across the entire study area from local hand pumps (LHP), *India Mark-II* hand pumps, so called common tube wells (CTW), open dug wells (ODW) and others (two submersible pumps, one deep tube well, one irrigation well and one pond). Since the depth of the wells (Rania: LHP and ODW 4 to 15 m, CTW 30 to 62 m; Chhiwali: ODW 7 to 11 m, LHP and CTW 31 to 76 m; Godhrauli: CTW 22 to 46 m) is relatively uniform for the well types, conclusions for the aquifers can be made. Concerning the objective of this study, three aspects were especially considered in the selection of the wells, (i) to assess the extent of the pollutant plumes, (ii) to study the influence of sampling depth, which conforms to different types of wells and (iii) to identify local specifics. The hand pumps were sampled from the outlets after flushing of about 30 L to remove stagnant water. The samples were immediately filtered through a 0.45 µm cellulose acetate filter (Merck) and collected in acid cleaned (conc. HNO_3, supra pure, Merck) polyethylene tubes without headspace. Sample aliquots were analyzed in-situ for Cr(VI) using a field test-kit (Merck Millipore), while other parameters like EC and speciation were recorded on unacidified samples in the laboratory. Although the samples were not acidified immediately on site, no precipitation occurred prior to the measurements. For each sample, well depth, well owner, and geographic coordinates were recorded. Additionally, the owners of the wells were consulted regarding the color and taste of the water during the course of the year.

2.4. Analyses of the physical and chemical composition of groundwater

Groundwater pH was measured potentiometrically after calibration using an ion-sensitive glass electrode (Aquatrode Plus, Methrom). The electric conductivity (EC) was determined using a conductivity probe (SevenEasy, Mettler-Toledo). For the determination of alkalinity, 5 mL of each sample was titrated with 0.1 M HCl to pH 8.2 and 4.3 using a Metrohm 775 Dosimat and a Metrohm 728 Stirrer. Chromium(VI) concentration was determined spectrophotometrically at 540 nm (Lambda 25 UV/Vis Spectrometer, PerkingElmer) according to the diphenylcarbazide method (US EPA 1992). The detection limit for Cr(VI) in samples was 0.005 mg L^{-1}. The concentrations of F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, and NO_3^- were determined by ion chromatography (ICS-1000, Dionex). Concentrations of Ca, K, Mg and Na were measured by flame atomic absorption spectrometry (AAS, iCE 3500, Thermo Scientific) with an air-acetylene flame, and total Cr (>1 mg L^{-1}) was determined with a nitrous oxide-acetylene flame. Nineteen elements (Si, Sr, Al, As, Ba, Cd, Co, Cr (<1 mg L^{-1}), Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, U, V and Zn) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, X-Series II, Thermo Scientific).

2.5. Statistical evaluation

Descriptive statistics were performed with the measured values of the samples collected in the pre-monsoon period and at the end of the monsoon period using Origin 8.5 (OriginLab). Statistical data evaluation was performed by the software IBM SPSS Statistics (Version 21). Basically, the nonparametric Spearman rank correlation coefficient was determined as a measure of the statistical dependency between variables, since some of the variables were not normally distributed. Significance was considered in circumstances where $p < 0.01$. A two sample t-Test assuming equal variances was applied to investigate if log-transformed Cr(VI) levels of the pre-monsoon and monsoon sampling campaigns differed significantly. The test was applied to the whole sample collectively and to sub-sample groups that accounted for the degree of contamination.

3. Results and discussion

3.1 Mapping of COPR dumpsites

Many of the COPR waste sites in Rania, Chhiwali, and Godhrauli are located in densely populated residential areas, in industrial or commercial areas, and in the vicinity of agricultural land (Figure 1). Details of the coordinates of these sample locations, the estimated area and the starting date and duration of landfill operations are provided in the supplementary material (Table S1). In Rania, the main COPR dumpsite (#E) covers an area of about 55,800 m^2 and is located opposite to a closed BCS manufacturing unit. The thickness of the COPR heaps is highly variable and is visually estimated to be between 0.5 and 1.5 m. The factory site itself also hosts huge quantities of COPR waste. Besides the main dumping site, several small waste sites are located along the road in Umran, where the COPR was partially used as a base material in road construction (#A). However, no COPR dumps could be identified in Khan Chandpur. In Chhiwali, the main COPR dumpsites have an area of about 2,100 m^2 (#H) and 8,100 m^2 (#K). Furthermore, several small dumpsites (< 350 m^2) are dispersed in this area either along the Kanpur – Allahabad highway or next to the side roads. Notably, in the case of dumpsite #H, parts of the village are directly located on the waste heap, which affects the people living there on an unimaginable scale. In Godhrauli, five COPR dumpsites with areas ranging from 100 to 5,200 m^2 could be identified. The dumpsites are located outside the village in an area of intensive agriculture. During the monsoon season, Cr is leached out from the COPR waste and flushed over the fields. Matern and Mansfeldt (2016) reported a Cr content of 0.54 g kg^{-1} in an agricultural soil close to the dumpsite #Q, of which about 9% was present in the mobile or exchangeable form.

3.2 Geochemical characteristics of groundwater

Table 1 shows the descriptive statistics of the investigated groundwater samples. For all analyzed solutes, except F^-, NO_3^-, As, Cr, Mo, Ni and U, the measured maximum values were below the drinking water guidelines set up by the WHO (2011), and are hence not discussed further. This also holds for Ni, which slightly exceeded the guideline value in one sample only (5% above WHO standard). Important parameters of the investigated wells in the study area (Table S2) as well as detailed element concentrations (Tables S3 and S4) are listed in the SM.

Fluoride contamination. Consumption of water with elevated F^- causes fluorosis, which is the most prevalent groundwater related disease in India (Mumtaz et al. 2015). Fluoride concentrations were found to be high in the study area, with maximum values of 6.3 mg L^{-1} (Rania), 33 mg L^{-1} (Chhiwali) and 10.9 mg L^{-1} (Godhrauli). Overall, 75% of the wells exceeded the guideline value of 1.5 mg L^{-1} (WHO, 2011). No differences in contamination were observed between the different types of wells. Altogether, F^- concentration in groundwater varies without any obvious trend, indicating a sporadic occurrence. Fluoride contamination has been found elsewhere in Uttar Pradesh (CGWB 2010) and has been related to the weathering of the Indo-Gangetic alluvium (Kumar and Saxena 2011). Raju et al. (2012) reported concentrations up to 6.7 mg L^{-1} in wells of the Sonbhadra district, Uttar Pradesh.

Nitrate contamination. Nitrate is considered to be relatively non-toxic. However, there is a risk of methemoglobinemia particularly to infants arising from elevated NO_3^- concentrations in drinking water (Fewtrell 2004). Maximum nitrate concentrations in the study area were 230 mg L^{-1} (Rania), 4,481 mg L^{-1} (Chhiwali) and 135 mg L^{-1} (Godhrauli), and the highest NO_3^- values (> 500 mg L^{-1}) were found in ODWs. In total, 25% of the wells exceeded the guideline value of 50 mg L^{-1} (WHO 2011) with wells in Chhiwali having higher incidence (71%) and severity of contamination. Elevated NO_3^- concentrations up to 375 mg L^{-1} have also been reported for Fatehpur district (CGWB 2010). Sankararamakrishnan et al. (2008) reported NO_3^- concentrations up to 735 mg L^{-1} in Kanpur Dehat district. Nevertheless, NO_3^- concentrations as high as measured in our study area have not been observed before in Uttar Pradesh. Nitrate contamination may arise from runoff from agricultural fields after excess application of nitrogen fertilizers, the disposal of untreated human or animal waste (Chakraborti et al. 2011), or the oxidation of organic nitrogen compounds in soil by chromate.

Arsenic contamination. Groundwater As contamination in the Ganga Plain is primarily observed in the floodplains, since its sources are the rivers originating from the Himalaya Mountains (Chakraborti et al. 2009). However, As concentrations in the upper Ganga plain are lower than reported for the middle and lower Ganga plain.

Table 1 Physical and chemical parameters of the groundwater[a] in Rania (n = 70), Chhiwali (n = 42), and Godhrauli (n = 15), as well as the guideline values set up by the WHO (2011).

	Unit	Rania			Chhiwali			Godhrauli			WHO
		Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	
pH	(–)	7.8	8.6	8.3	7.7	8.7	8.3	7.7	8.6	8.3	n.v.[b]
EC[c]	(mS cm^{-1})	0.6	4.6	1.1	0.8	16.2	2.4	1.0	2.6	1.6	2.5[d]
Alkalinity	(mmol L^{-1})	6.3	25.1	9.1	6.9	39.3	12.3	7.1	15.6	12.0	n.v.
Cr(VI)	(mg L^{-1})	LDL[e]	34.8	0.01	LDL	115	0.01	LDL	1.99	0.30	0.05
Cr(III)	(mg L^{-1})	LDL	5.63	LDL	LDL	6.30	LDL	LDL	0.36	LDL	0.05
Cl^-	(mg L^{-1})	9.85	486	57.5	12.11	1616	213	66.4	235	120	n.v.
F^-	(mg L^{-1})	LDL	6.31	2.04	LDL	33.1	1.77	0.69	10.9	3.65	1.50
NO_3^-	(mg L^{-1})	LDL	230	4.51	LDL	4481	137	LDL	135	34.5	50
SO_4^{2-}	(mg L^{-1})	2.59	369	52.8	3.68	2301	228	394	351	126	n.v.
Ca	(mg L^{-1})	4.87	157	52.8	8.77	283	54.6	16.5	83.2	52.6	n.v.
K	(mg L^{-1})	2.02	776	4.52	1.00	3289	7.69	8.62	105	25.3	n.v.
Mg	(mg L^{-1})	9.99	107	39.9	6.84	429	49.9	11.9	88.5	54.9	n.v.
Na	(mg L^{-1})	40.8	427	97.2	45.7	991	305	81.3	407	142	n.v.
Si	(mg L^{-1})	6.69	35.3	12.8	10.2	23.4	15.9	8.02	22.2	13.4	n.v.
Sr	(mg L^{-1})	0.23	2.99	1.13	0.22	9.50	1.39	0.35	5.75	2.10	n.v.
Al	(µg L^{-1})	LDL	13.5	LDL	LDL	26.0	LDL	LDL	16.0	LDL	n.v.
As	(µg L^{-1})	LDL	50.5	0.5	LDL	74.5	1.5	LDL	12.5	0.5	10
Ba	(µg L^{-1})	19.0	400	99.8	15.0	319	53.5	36.0	410	117	700
Co	(µg L^{-1})	LDL	1.0	LDL	LDL	1.5	LDL	LDL	0.5	LDL	n.v.
Cu	(µg L^{-1})	LDL	20.5	0.5	LDL	14.0	1.5	LDL	5.0	1.0	2000
Fe	(µg L^{-1})	LDL	38.0	2.0	LDL	85.5	4.0	0.5	102	3.5	n.v.
Mn	(µg L^{-1})	LDL	970	5.5	LDL	940	7.5	LDL	106	8.5	n.v.
Mo	(µg L^{-1})	1.0	364	7.0	1.5	1900	22.0	2.5	34.5	18.5	70[f]
Ni	(µg L^{-1})	LDL	73.0	0.5	LDL	9.5	0.5	LDL	2.5	1.0	70
Pb	(µg L^{-1})	LDL	1.5	LDL	LDL	1.0	LDL	LDL	2.5	LDL	10
Sb	(µg L^{-1})	LDL	3.0	10.0	0.5	2.5	1.0	0.5	8.5	1.0	20
Se	(µg L^{-1})	LDL	18.5	1.5	0.5	32.5	3.5	LDL	12.5	2.0	40
U	(µg L^{-1})	2.0	115	24.3	14.0	350	66.5	8.0	108	54.0	30
V	(µg L^{-1})	3.0	72.0	9.0	1.5	63.0	8.0	1.0	9.0	5.5	n.v.
Zn	(µg L^{-1})	LDL	1323	12.5	LDL	690	19.3	2.0	1629	68.0	n.v.

[a] NO_2^-, PO_4^{3-} and Cd are below the analytical detection limit and thus not listed.

[b] n.v., no formal guideline value

[c] EC, electric conductivity

[d] according to European Union (Drinking Water) Regulations 2014

[e] LDL, lower detection limit

[f] health-based value

Arsenic is classified by the International Agency of Research on Cancer (IARC) as a class I carcinogen that exhibits acute and chronic toxicity depending on the type of exposure (Hettick et al. 2015). Hence, the WHO (2011) has set up a guideline value of 10 µg L^{-1}. Arsenic concentrations were elevated in 11% of the wells with maximum concentrations of 51 µg L^{-1} (Rania), 75 µg L^{-1} (Chhiwali) and 13 µg L^{-1} (Godhrauli), and predominantly present in the upper aquifer up to a depth of 12 m. Chakraborti et al. (2009) reported As concentrations up to 707 µg L^{-1} for the adjacent Allahabad district. In the same study, 66% of the wells contained As above the WHO guideline value and As contamination mostly occurred in shallow hand tube-wells (depth 7.5 to 40 m).

Molybdenum contamination. Molybdenum is an essential trace element for plants, animals and humans (Gupta 1997); however, ruminants may develop molybdenosis, a Mo-induced copper deficiency at higher consumption (Underwood 1976). Furthermore, chronic oral exposure can result in gastrointestinal disturbances, growth retardation, anemia, hypothyroidism, bone and joint deformities, sterility, liver and kidney abnormalities (Afkhami et al. 2009). Molybdenum concentrations were elevated in 16% of the investigated wells with maximum concentrations of 364 µg L^{-1} (Rania), 1,900 µg L^{-1} (Chhiwali) and 35 µg L^{-1} (Godhrauli), compared to the health-based guideline value being 35 µg L^{-1} (WHO 2011). Elevated Mo levels were restricted to ODWs. To the best of our knowledge, elevated Mo concentrations have not been reported previously for any parts of Uttar Pradesh. Elevated Mo concentrations are possibly derived from weathering of black shales of the Himalayas (Rahaman et al. 2010).

Uranium contamination. Exposure to U can cause both radiological as well as chemical toxicity, e.g. nephrotoxicity, although the chemical toxicity is more relevant here (Kurttio et al. 2006). Uranium concentrations were found to be high in the study area, with maximum values of 115 µg L^{-1} (Rania), 350 µg L^{-1} (Chhiwali) and 108 µg L^{-1} (Godhrauli). Altogether, 59% of the wells exceeded the WHO guideline value of 30 µg L^{-1}. These values are distinctly higher than reported by Kumar et al. (2015) who found U concentrations up to 63 µg L^{-1} in Uttar Pradesh, with the maximum U value for Fatehpur being 36 µg L^{-1}. Higher U concentrations were found in the state of Punjab, North India, with maximum U values of 579 µg L^{-1} (Bajwa et al. 2015). The reason for elevated U concentrations is unexplained, but local mineralogical composition may be the contributing factor (Kumar et al. 2015).

Problem of salinity. Groundwater salinity is a growing problem in several Indian states (Chakraborti et al. 2011). In Uttar Pradesh, instances of salinity have been reported previously, resulting mainly from excessive groundwater use for irrigation (Chakraborti et al. 2011). The WHO has not established a guideline value for salinity, but water with an EC up to 2.5 mS cm^{-1} is drinkable according to European Union (drinking water) regulations (2014). The Bureau of Indian Standards (BIS 2009) has recommended a drinking water standard for salinity of 0.75 mS cm^{-1} that can be increased to 3.0 mS cm^{-1} in case of no alternate source. Relatively high values of EC were found in the study area with a maximum of 4.6 mS cm^{-1} (Rania), 16.2 mS cm^{-1} (Chhiwali) and 2.6 mS cm^{-1} (Godhrauli), although the ODWs were more affected than the other wells. Wells with elevated EC values higher than 2.5 mS cm^{-1} are marked in blue in Fig. 1. Overall, 17% of the wells showed EC values above the guideline value. However, 70% of the affected wells were placed in Chhiwali. Thus far, only local spots with EC values above 3.0 mS cm^{-1} have been reported for some districts in Uttar Pradesh (CGWB 2010). Elevated values of EC are not attributed to the COPR dumps, since they are also observed in wells located in areas unaffected by COPR. Indeed, high Cr(VI) concentrations lead to elevated EC values from 1 to 2 mS cm^{-1}, the highest EC values (2.5 to 16 mS cm^{-1}) were found in samples being totally uncontaminated with Cr.

Main cations and anions. Solutes like Cl^-, SO_4^{2-}, Ca, K, Mg and Na are not a significant risk for human health even at higher concentrations as long as the salinity does not exceed critical values. However, they are important parameters for identifying the groundwater characteristics and tracking any temporal changes in the chemical composition of groundwater. The highest values of the aforementioned elements were found in wells in Chhiwali (Table S4). Open dug wells with depths around 11 m were more affected than other wells, although one CTW (55 m) and one submersible pump (91 m) also showed high Cl^-, SO_4^{2-}, and Na values.

3.3 Cr(VI) distribution in the groundwater

Figure 1 and Table S3 of the SM show the Cr(VI) distribution in the investigated samples. The samples were classified according to their total Cr concentrations; as highly contaminated (Cr > 1 mg L^{-1}, red), moderately contaminated (0.05 mg L^{-1} < Cr < 1 mg L^{-1}, orange), and uncontaminated (Cr < 0.05 mg L^{-1}, green).

Chromium(VI) concentrations in Rania ranged from below the detection limit (LDL) up to 35 mg L^{-1}. High Cr(VI) concentrations were mainly present in LHPs and CTWs but not in OWDs. However, even deeper aquifers (well #29) seem to be contaminated, with Cr(VI) concentrations up to 2.47 mg L^{-1} at 175 m depth. Overall, 21% of the wells were moderately contaminated and 28% were highly contaminated, with the highest Cr(VI) concentrations being found close to main COPR dumping site (23 mg L^{-1}), northward along the street in Umran (35 mg L^{-1}) and in the village Khan Chandpur (30 mg L^{-1}) lying approximately 2 km south of the main dumping site (#E). Chromium(III) concentrations were found to be distinctly lower (up to 5.6 mg L^{-1}) and were correlated with Cr(VI) concentrations. Since Cr(III) is not leached from COPR in significant amounts (data not shown) incidence of Cr(III) may point to a partial Cr(VI) reduction in the vadose zone or in the groundwater as well as the oxidation of organic material in soils by Cr(VI). Farmer et al. (2002) reported Cr(VI) reduction by humic substances and the formation of Cr(III)–humic complexes in COPR affected groundwater in Glasgow. However, Cr(III) associated with organic material in groundwater was site-specific in the Glasgow study. The villages Prasidhpur (1 km east of the dumpsite), Bilsarayan (3 km south of the dumpsite) and the western part of Umran were uncontaminated. The high Cr(VI) levels in the wells south of the highway and north of Khan Chandpur could not be related to the presence of COPR dumpsites located in direct vicinity. We therefore hypothesize that the well contamination stems from a Cr(VI) plume spreading in south-southeastern direction from the main dumpsite north of the highway. If this were the case, the plume would have covered a distance of 1 km approximately since the operation of the dumpsite was initiated. The direction of groundwater flow and the rate of plume spreading were confirmed by the determination of the hydraulic gradient. Therefore, we used the piezometric levels and GPS-coordinates of ODW between ~3 and ~1.5 km apart from one another, with one ODW located in the village of Khan Chandpur (Table S5). Evaluation of the hydraulic triangle gave a regional maximum hydraulic gradient of 0.000537 m/m with a south southeastern groundwater flow direction. Assuming a saturated hydraulic conductivity of 10^{-3} m/s and a porosity of 0.5 m^3/m^3, this yields a pore water velocity of 0.093 m/day. Neglecting both adsorption of chromate and anion exclusion, this is equivalent to a thirty-years-travelling distance of 1 km approximately. Since COPR production in Rania started in the late 1980s this provides a strong indication for the dumpsite as the cause of an advancing a Cr(VI) plume. The main dumpsite is considered to be in the center of the plume, showing the highest Cr(VI) concentrations up to 80 mg L^{-1}, measured in a piezometer that is installed in the dumpsite (Singh et al. 2013). Most probably, the contamination north of Umran is to be considered as disconnected from this plume and some smaller heaps were found along the roadside. Singh et al. (2013) investigated 21 wells in this area and reported a similar Cr(VI) distribution in Rania, but Cr(VI) concentrations northward along the street in Umran never exceeded 1.5 mg L^{-1}. In general, Cr(VI) distribution varied on a small-scale, e.g., two LHPs with the same depth, which were located in the northern part of Umran and separated by ~10 m, had Cr(VI) concentrations of 0.21 (moderately contaminated) and 3.95 mg L^{-1} (highly contaminated).

In Chhiwali, Cr(VI) concentrations ranged from LDL to 115 mg L^{-1}, although highly contaminated wells were only found adjacent to the dumping sites. Chromium(III) concentrations in groundwater were also distinctly lower with a maximum value of 6.3 mg L^{-1}. Overall, 17 % of the wells were moderately contaminated and 8% of the wells were highly contaminated. Furthermore, Cr(VI) contamination seems to be restricted to the upper aquifers, since no elevated Cr(VI) concentration were found below 40 m depth (Table S3 of the SM). Small scale variability of the contamination was also observed here, but as opposed to Rania, no plume could be identified. Wells in the northeast and southwest of the dumpsite (#K) did not have elevated

Cr(VI) concentrations, however one well had a slightly elevated Cr(III) concentration (0.085 mg L^{-1}). No Cr(VI) contamination was observed in the southeastern part of the study area of Chhiwali. Even the CTW located adjacent to the BCS manufacturing unit was uncontaminated. Contamination in the northwestern parts of Chhiwali seems bounded by a river and an inflow of Cr(VI) contaminated water into the river cannot be excluded.

In Godhrauli, 13% of the wells were moderately contaminated and 38% were highly contaminated with Cr(VI) concentrations ranging from LDL to 2.0 mg L^{-1}. As reported by the villagers, visually the Cr(VI) concentration of the moderately contaminated wells seems to increase at higher water usage. The data suggests that wells installed at a depth of ~22 m were more contaminated than deeper wells (> 30 m), although the number of samples is too low for any definitive conclusion. As described for Chhiwali, Cr(VI) contaminated water was found close to the dumping sites and not elsewhere in this area.

Altogether, the Cr(VI) concentrations in the three investigated areas are in the range of the concentration reported for Glasgow and New Jersey (Burke et al. 1991; Farmer et al. 2002). However, the maximum value found in Chhiwali is, according to our knowledge, distinctly higher than reported elsewhere in the world.

3.4 Correlation of selected parameters

Correlation coefficient of selected parameters indicated strong positive correlation between Cr(VI) and Cr(III) in the entire study area (Table 2). Chromium(VI) inflow arises from leaching of COPR dumpsites and is potentially at least partly reduced to Cr(III) by soil compounds during percolation though the subsurface. The association between As-Mo-U arises from the geogenic source of these metals, since there is no known anthropogenic source, which can contribute to this type of association in the study area. No significant correlations that were valid for the entire study area were found for F^- and NO_3^-. However, a high correlation exits in the Godhrauli area for NO_3^- and Cr(VI), as well as Cr(III). Although this correlation is difficult to explain, some works reported a link between Cr(VI) reduction and the presence of NO_3^-. Han et al. (2010) found an increase in chromate reduction when denitrification was high presumably because metabolites increased. These metabolites are used by chromate-reducing bacteria as electron donator, which seemed to be the link between nitrate and chromate. It should be noted that in the study area many specifics exist and overlap, which makes correlation, in general, difficult.

Table 2 Spearman rank correlation coefficient (r_S) of selected parameters. Significance was considered in circumstances where $p < 0.01$.

		Moderate correlation (r_S = 0.5 to 0.7)	High correlation (r_S = 0.7 to 0.9)
F^-	Rania	n.c.[a]	
	Chhiwali	Ca, Mg, Sr, Mn	
	Godhrauli	Na	K, Se
NO_3^-	Rania	n.c.	
	Chhiwali	pH, Mg, Sr	EC, Cl^-, SO_4^{2-}
	Godhrauli	n.c.	Cr(VI), Cr(III)
As	Rania	Alkalinity, Na, Mo	
	Chhiwali	EC, Alkalinity, Cl^-, SO_4^{2-}, Na, Al, U	Mo, V
	Godhrauli	Ba	Sb
Cr(VI)	Rania	Cl^-, SO_4^{2-}, Fe	Cr(III)
	Chhiwali	Cr(III)	
	Godhrauli	n.c.	Cr(III), NO_3^-
Mo	Rania	Alkalinity, As	
	Chhiwali	EC, Alkalinity, Cl^-, SO_4^{2-}, Na, U, V	As
	Godhrauli	Co	
U	Rania	EC, Alkalinity, Na, Se, V	
	Chhiwali	EC, Alkalinity, Cl^-, Na, As, Mo, V	
	Godhrauli	Mg	EC, Alkalinity
EC[b]	Rania	U	Alkalinity, Cl^-, SO_4^{2-}, Na
	Chhiwali	Alkalinity, K, Mg, As, Mo, Se, Sr, U, V	Cl^-, SO_4^{2-}, NO_3^-, Na
	Godhrauli	Si	Alkalinity, Cl^-, SO_4^{2-}, Mg, Sr, U

[a] $r_S < 0.5$

[b] EC, electric conductivity

3.5 Influence of monsoon precipitation

Results of the t-test revealed no significant effect of the pre-monsoon and monsoon periods on groundwater contamination by Cr(VI). This is supported by the fact that Cr(VI) concentration increased in some wells in the monsoon season while in others it decreased (Table 3 and S3). Median values were relatively unaffected by sampling season (Table 3). This holds for wells with Cr(VI) concentrations above the guideline value, where 11 wells had higher and 10 wells had lower Cr(VI) concentrations in the monsoon compared to the pre-monsoon season.

In the design of the study we hypothesized that monsoon precipitation drives the influx of Cr(VI) from the COPR dumpsites to the center of contaminant plumes and possibly has a diluting effect at the plume fringes. However, this could not be confirmed. A possible reason could be the weak southwest monsoon season rainfall over India in 2014 (IMD 2015b). Seasonal rainfall was lower than normal in most parts of the country. Uttar Pradesh received less than 42% of the long-term average from 01.06.2014 to 30.09.2014 (IMD 2015b). Precipitation varied regionally resulting in even lower rainfall percentages in the districts Fatehpur (-68%) and Kanpur Dehat (-73%) (IMD 2015a). Furthermore, the time-scales of infiltration and onward transport to the sampled locations may be larger than the two- month monsoonal period considered in this study. In the investigated period, the seasonality of Cr(VI) levels may thus rather be attributed to other factors including (i) diurnal variations, (ii) irrigation effects, and (iii) replacement of water in ODWs. Diurnal variations in the individual wells seem to be dependent on water consumption. Some villagers reported that the water is apparently clean in the morning (colorless) and turns to be contaminated (yellowish) after longer use in the evening. This effect could bias the sample data since it was not possible to collect the samples at the same time of the day in the two sampling periods. The effects of irrigation are closely related to diurnal variations since irrigation greatly increases the actual water demand. In response to visually discernible contamination, in some cases the villagers replaced the water in the ODWs. Obviously, water was only initially clean, but turned contaminated within weeks. Under such conditions observed Cr(VI) levels may not be representative depending on the time span between water replacement and sampling Cr(VI) levels. Altogether, it can be assumed that hydraulic windows exist between the different groundwater stories, e.g. when well drilling was inappropriate. Thus, wells providing water from uncontaminated aquifers may deliver contaminated water when consumption is high and contaminated aquifers are tapped.

Table 3 Cr(VI) concentration in mg L^{-1} in pre-monsoon and monsoon seasons and number of wells with increasing and decreasing Cr(VI) concentration during the monsoon season.[a]

	Median		Max		Number of wells[b]	
	pre-monsoon	monsoon	pre-monsoon	monsoon	increasing Cr(VI) conc.	decreasing Cr(VI) conc.
Rania	0.007	0.008	33.9	30.3	4	7
Chhiwali	<0.005	0.011	78.3	115	5	1
Godhrauli	0.401	0.304	1.83	2.00	2	2

[a] only the wells investigated in both seasons were considered

[b] only wells with Cr(VI) concentration above 0.05 mg L^{-1} were considered

It is noticeable that most of the wells showed decreased Ca and increased Mg concentrations during the monsoon season (Table S6), for which we do not have any explanations yet. However, no significant effect of the pre-monsoon and monsoon could be observed for Cl^-, SO_4^{2-}, K, and Na.

4. Conclusion and recommendations

Field sampling results showed that 95% of the sampled wells of the study area do not provide safe drinking water. Most samples exhibited multiple contamination with various elements and compounds exceeding international threshold values. Although F^-, NO_3^-, As, Mo, and U were found to be elevated in most of the investigated wells, Cr(VI) constitutes the most prominent hazard due to its acute toxicity and exceptionally high concentrations. The severity of Cr contamination could be gauged from the incidence of 19% of the wells that were classified as moderately contaminated and 23% as highly contaminated. The measured concentration of 115 mg L^{-1} in Chhiwali was higher than for COPR affected groundwater bodies elsewhere in the world. A total of 17 COPR dumps were identified as sources of Cr(VI) groundwater contamination. Although the influence of monsoon precipitation on Cr(VI) mobilization from the dumpsites could not be established, this study clearly highlights the necessity of immediate monitoring of the identified contaminants. Monitoring of major components (Na, K, Ca, Mg, Cl^-, SO_4^{2-} and HCO_3^-) as well as hydrogen and oxygen stable isotopes may also be useful in order to identify the geochemical characteristics in water, including the temporal variability, and the connection between surface-water and groundwater. There is an urgent need to inform the villagers about the danger of drinking the contaminated water. Color-coding of the contaminated wells may be helpful in this context. Remediation of the contaminated groundwater may provide clean water to the local population on the medium term only. Therefore, interim solutions should be sought for. These could range from simple, yet robust, water treatment methods applicable at the level of individual households to the provision of safe drinking water by pipelines. The main COPR dumpsites must be remediated either in situ by encapsulation/stabilization or by disposal to a hazardous waste landfill.

This study is a first in-depth report on the reach of groundwater pollution at the COPR dumpsites around Kanpur based on a screening of potentially affected wells. Given this, some aspects remain tentative regarding the hydrogeological setting that should be addressed in future research. The use of multilevel sampling techniques and a better characterization of the downgradient transport are among the primary issues asides a solution for the safe water supply of the residents.

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Supplementary material

Spatial distribution of Cr(VI) groundwater contaminated by Chromite Ore Processing Residue (COPR) dumpsites during pre-monsoon and monsoon season

Table S1 COPR sites identified in Rania, Chhiwali and Ghodrauli. n.d., not determined.

Site number	Sample location	Coordinates (dd°mm'ss.s")	Estimated area (m^2)	Time of landfill
A	Rania	N 26°24'42.2" E 80°02'16.1"	n.d.	late 1980s to 2005
B	Rania	N 26°24'34.9" E 80°02'24.3"	450	late 1980s to 2005
C	Rania	N 26°24'29.4" E 80°02'29.9"	100	late 1980s to 2005
D	Rania	N 26°24'25.7" E 80°02'35.3"	3,800	late 1980s to 2005
E	Rania	N 26°24’12.4” E 80°02’51.2”	55,800	late 1980s to 2005
F	Chhiwali	N 26°12’04.0” E 80°32’07.5”	100	since 2004
G	Chhiwali	N 26°12’01.2” E 80°32’10.0”	100	since 2004
H	Chhiwali	N 26°11’45.8” E 80°32’21.3”	2,100	2004-2008
I	Chhiwali	N 26°11’54.2” E 80°32’21.8”	100	since 2004
J	Chhiwali	N 26°11’59.6” E 80°32’33.0”	100	since 2004
K	Chhiwali	N 26°11’42.9” E 80°33’11.8”	8,100	2004-2008
L	Chhiwali	N 26°11’15.6” E 80°33’14.5”	350	since 2004
M	Godhrauli	N 26°08'44.4" E 80°34'05.3"	1,600	since 2004
N	Godhrauli	N 26°08'34.0" E 80°34'02.3"	100	since 2004
O	Godhrauli	N 26°08'25.6" E 80°33'57.4"	100	since 2004
P	Godhrauli	N 26°08'22.5" E 80°33'56.3"	3,300	since 2004
Q	Godhrauli	N 26°08'20.3" E 80°33'45.8"	5,200	since 2004

Table S2 Important parameters of the investigated wells in the study area. EC, electric conductivity; CTW, common tube well; LHP, local hand pump; ODW, open dug well; DTW, deep tube well; n.d., not determined; n.i., no information

Sample ID	Coordinates (dd°mm'ss.s")	Owner	Type	Estimated depth of the wells (m)	EC pre-monsoon (mS cm^{-1})	EC monsoon (mS cm^{-1})
Rania						
1	26°23'36.1" 80°02'26.3"	Suresh Chandra	CTW	37	0.85	0.83
2	26°24'03.3" 80°02'09.6"	Prem Narain	CTW	49	0.62	0.61
3	26°24'01.7" 80°02'11.3"	Kripal Yadav	LHP	12	1.42	1.49
4	26°24'09.8" 80°02'06.3"	Shiv Raj Singh	ODW	6	4.58	3.20
5	26°24'14.0" 80°02'03.3"	Public	ODW	10	n.d.	0.82
6	26°24'16.9" 80°02'04.2"	Public	ODW	6	n.d.	2.81
7	26°24'24.4" 80°02'37.0"	Perfect Security Gower. Office (Subhash Yadav)	LHP	12	0.87	0.93
8	26°24'28.9" 80°02'14.5"	Ram Gopal	ODW	4	3.28	2.67
9	26°24'28.2" 80°02'15.3"	Shri Krishna	CTW	30	0.76	0.75
10	26°24'29.9" 80°02'29.9"	Charan Singh	LHP	11	0.79	0.78
11	26°24'48.6" 80°02'08.6"	Suresh Kumar	LHP	12	1.69	1.71
12	26°24'47.7" 80°02'09.2"	Gani Mohammad	LHP	12	n.d.	1.53
13	26°24'46.9" 80°02'08.8"	Absar Ali	LHP	12	n.d.	1.15
14	26°24'46.7" 80°02'08.8"	Absar Ali	LHP	13	n.d.	0.97
15	26°24'48.6" 80°02'08.2"	Munna Singh	CTW	37	1.05	1.04
16	26°25'12.3" 80°02'27.1"	Mamta	LHP	12	1.00	1.00
17	26°23'58.1" 80°02'58.1"	Major Virendra Singh	CTW	53	1.97	1.92
18	26°23'58.6" 80°02'57.7"	Sanjay Yadav	LHP	50	1.37	1.24
19	26°24'20.5" 80°02'41.1"	Mahesh Chandra Tripathi	LHP	12	n.d.	1.83
20	26°24'20.8" 80°02'41.0"	Shailendra Tripathi	LHP	12	n.d.	0.89

Sample ID	Coordinates (dd°mm'ss.s")	Owner	Type	Estimated depth of the wells (m)	EC pre-monsoon (mS cm^{-1})	EC monsoon (mS cm^{-1})
21	26°23'56.8" 80°02'56.8"	Virendra Singh	sub-mersible pump	37	n.d.	1.11
22	26°23'56.7" 80°02'54.7"	Dinesh	LHP	11	n.d.	1.77
23	26°23'57.1" 80°02'58.4"	Krisha Gopal	LHP	46	n.d.	1.72
24	26°24'06.0" 80°03'28.0"	M.D. Computerised Dharam Kanta	LHP	n.i.	1.00	n.d.
25	26°24'06.1" 80°03'29.6"	Lalbahadur	LHP	12	n.d.	1.40
26	26°24'31.3" 80°03'20.6"	Kailash Chandra Sharma	CTW	37	1.03	1.01
27	26°24'28.8" 80°03'12.6"	Pandit Rambabu Sharma	ODW	5	2.02	0.94
28	26°23'41.4" 80°03'23.8"	Shivlal Singh	LHP	13	0.84	0.84
29	26°23'35.3" 80°03'04.8"	Goverment	DTW	175	0.98	0.95
30	26°23'46.1" 80°02'45.6"	Naresh Singh	CTW	62	1.21	n.d.
31	26°23'46.7" 80°02'44.8"	Naresh Singh	CTW	37	n.d.	0.75
32	26°23'44.5" 80°03'02.2"	Ram Kumar /Parrot	LHP	13	1.77	1.85
33	26°23'45.0" 80°03'01.6"	Ashok Kumar	CTW	43	1.15	1.36
34	26°23'47.9" 80°02'59.0"	Gyan Singh	CTW	37	1.09	1.55
35	26°23'47.2" 80°02'59.6"	Dharmendra Katedar	LHP	12	1.63	1.60
36	26°23'35.5" 80°03'01.5"	Gyanendra Veer Singh	CTW	37	0.86	0.86
37	26°23'36.3" 80°03'01.5"	Ram Nath	LHP	13	1.05	1.04
38	26°23'30.0" 80°03'04.5"	Goverment	CTW	32	0.76	0.74
39	26°22'44.4" 80°02'56.2"	Haneef	CTW	37	1.07	1.01
40	26°22'42.2" 80°02'56.1"	Mannu	LHP	14	1.23	1.14
41	26°23'39.4" 80°02'34.1"	Vicky (Wearhouse)	CTW	43	0.75	0.71
42	26°23'48.2" 80°03'00.5"	Surendra	CTW	46	n.d.	2.09
43	26°23'48.5" 80°02'59.2"	Surendra	LHP	14	n.d.	1.94

Sample ID	Coordinates (dd°mm'ss.s")	Owner	Type	Estimated depth of the wells (m)	EC pre-monsoon (mS cm^{-1})	EC monsoon (mS cm^{-1})
Chhiwali						
44	26°11'45.2" 80°32'21.6"	Ali Hussain	CTW	76	1.57	1.58
45	26°11'46.5" 80°32'19.5"	Pratap Narain Baislai	LHP	37	1.71	1.90
46	26°11'46.8" 80°32'18.9"	Samar Jeet Singh	CTW	55	4.51	2.45
47	26°11'44.9" 80°32'16.1"	Virender Singh	submersible pump	91	3.16	3.27
48	26°11'44.2" 80°32'15.4"	Suraj Bhan Singh	ODW	11	3.43	3.18
49	26°11'44.0" 80°32'14.8"	Public	CTW	41	n.d.	1.57
50	26°11'46.8" 80°32'16.3"	Pradeep Kumar Tiwari	ODW	10	6.23	5.45
51	26°11'48.9" 80°32'15.1"	Mahendra Parihas	ODW	8	2.13	2.46
52	26°11'49.2" 80°32'16.1"	Narendra	LHP	40	0.81	0.79
53	26°11'51.1" 80°32'17.6"	Narendra Singh	ODW	10	4.23	3.33
54	26°11'49.5" 80°32'18.9"	Dapur	ODW	11	6.41	4.31
55	26°11'48.7" 80°32'18.7"	Radhe Shyam	ODW	11	4.67	3.58
56	26°11'36.4" 80°32'57.5"	Kallu	CTW	39	1.16	1.17
57	26°11'38.2" 80°33'03.1"	Parvez Farm	CTW	31	1.67	2.81
58	26°11'43.6" 80°33'17.0"	Jai Shankar Prasad Tiwari	ODW	12	2.00	2.30
59	26°11'46.0" 80°33'24.0"	Nand Kishore Dixit	CTW	26	2.20	2.08
60	26°11'47.7" 80°33'24.7"	Vijay Shankar Tiwari	ODW	11	14.3	12.5
61	26°11'48.1" 80°33'30.8"	Shyamu	ODW	7	8.03	n.d.
62	26°11'51.7" 80°33'32.5"	Public	CTW	32	n.d.	1.14
63	26°11'47.0" 80°33'31.1"	Manzil Singh Chauhan	ODW	11	16.2	15.4
64	26°10'50.5" 80°32'33.7"	Shobha Singh	CTW	34	1.08	n.d.
65	26°10'49.5" 80°32'32.5"	Ram Kumar	CTW	41	n.d.	1.15
66	26°11'06.7" 80°32'54.8"	Owner factory	CTW	55	0.94	0.95
67	26°11'40.8" 80°32'19.2"	–	Irrigation inflow	–	1.33	n.d.

Sample ID	Coordinates	Owner	Type	Estimated depth of the wells	EC pre-monsoon	EC monsoon
	(dd°mm'ss.s")			(m)	(mS cm^{-1})	(mS cm^{-1})
Godhrauli						
68	26°08'50.7" 80°34'09.7"	Public	CTW	34	1.48	1.35
69	26°08'53.4" 80°34'11.5"	Ramesh Singh	CTW	22	2.50	2.63
70	26°08'54.0" 80°34'11.7"	Raj Bahadur Singh	CTW	46	1.63	1.52
71	26°08'50.8" 80°34'03.3"	Ram Krishna	CTW	42	1.02	1.00
72	26°08'51.0" 80°34'04.6"	Rajole Chauhan	CTW	22	1.61	1.67
73	26°08'50.7" 80°34'04.3"	Public	ODW	12	n.d.	1.82
74	26°08'49.8" 80°34'02.5"	Public	pond	–	1.19	1.01
75	26°08'33.3" 80°33'52.1"	–	irrigation well	–	1.91	2.19

Table S3 Element concentrations of the investigated wells in the study area. n.d., not determined; pre-m., pre-monsoon; m., monsoon.

Sample ID	Cr(VI) pre-m.	Cr(VI) m.	F^- pre-m.	F^- m.	$\mathrm{NO_3}^-$ pre-m.	$\mathrm{NO_3}^-$ m.	As pre-m.	As m.	Mo pre-m.	Mo m.	U pre-m.	U m.
	(mg L^{-1})						(µg L^{-1})					
Rania												
1	<0.005	<0.005	0.8	2.6	<0.01	7.4	0.5	0.5	3.5	4.0	26.5	24.0
2	<0.005	<0.005	0.7	1.4	11.1	8.9	0.5	0.5	2.0	1.5	19.0	18.0
3	<0.005	0.007	<0.01	<0.01	<0.01	2.0	26.5	36.5	27.0	29.0	2.5	2.0
4	0.007	0.013	<0.01	<0.01	230	141	37.0	11.5	364	152	55.5	29.5
5	n.d.	0.021	n.d.	<0.01	n.d.	1.3	n.d.	5.0	n.d.	23.5	n.d.	2.5
6	n.d.	0.020	n.d.	<0.01	n.d.	138	n.d.	26.5	n.d.	213	n.d.	8.0
7	0.591	0.496	1.0	2.6	20.4	21.2	0.5	0.5	1.5	1.5	22.0	17.0
8	0.002	0.008	1.6	<0.01	62.7	6.9	8.0	50.5	20.5	4.5	108	19.5
9	<0.005	<0.005	0.6	2.2	32.0	32.9	<0.1	0.5	2.0	2.0	50.0	16.0
10	0.568	0.453	1.1	2.5	<0.01	5.3	0.5	0.5	5.5	5.0	18.5	12.0
11	6.16	4.29	0.9	2.5	25.4	23.6	0.5	0.5	7.0	5.5	57.0	53.5
12	n.d.	34.8	n.d.	3.2	n.d.	35.0	n.d.	0.5	n.d.	5.5	n.d.	34.0
13	n.d.	3.95	n.d.	2.1	n.d.	21.6	n.d.	0.5	n.d.	7.5	n.d.	31.5
14	n.d.	0.213	n.d.	4.8	n.d.	17.1	n.d.	0.5	n.d.	6.0	n.d.	17.5
15	0.007	0.009	1.0	2.6	84.7	82.9	1.5	1.0	37.5	7.0	29.0	19.5
16	<0.005	<0.005	2.3	3.6	4.9	<0.01	2.5	1.0	70.5	14.0	51.0	34.0
17	0.012	0.080	3.3	6.3	<0.01	<0.01	1.0	2.5	6.5	40.0	101	64.5
18	0.041	0.578	2.8	4.3	<0.01	<0.01	0.5	3.0	12.5	65.5	86.0	50.0
19	n.d.	23.0	n.d.	3.8	n.d.	<0.01	n.d.	0.5	n.d.	1.0	n.d.	17.0
20	n.d.	0.113	n.d.	2.1	n.d.	<0.01	n.d.	0.5	n.d.	1.5	n.d.	20.0

Sample ID	Cr(VI) pre-m.	Cr(VI) m.	F^- pre-m.	F^- m.	NO_3^- pre-m.	NO_3^- m.	As pre-m.	As m.	Mo pre-m.	Mo m.	U pre-m.	U m.
	(mg L^{-1})						(µg L^{-1})					
Rania												
21	n.d.	1.52	n.d.	2.8	n.d.	<0.01	n.d.	0.5	n.d.	16.0	n.d.	43.0
22	n.d.	0.697	n.d.	2.8	n.d.	<0.01	n.d.	0.5	n.d.	14.0	n.d.	21.0
23	n.d.	<0.005	n.d.	2.7	n.d.	<0.01	n.d.	3.0	n.d.	38.5	n.d.	62.5
24	<0.005	n.d.	0.7	n.d.	<0.01	n.d.	0.5	n.d.	1.5	n.d.	9.0	n.d.
25	n.d.	<0.005	n.d.	2.2	n.d.	<0.01	n.d.	0.5	n.d.	1.0	n.d.	10.5
26	<0.005	<0.005	3.4	3.9	<0.01	<0.01	2.5	2.5	39.5	41.0	50.0	33.5
27	0.007	<0.005	1.3	3.6	<0.01	<0.01	2.5	1.5	38.5	4.5	115	27.0
28	<0.005	<0.005	0.7	2.3	11.3	<0.01	2.0	1.0	10.0	2.0	19.5	10.0
29	2.47	1.74	0.8	2.4	<0.01	<0.01	1.0	0.5	5.5	4.5	24.5	22.0
30	3.53	n.d.	0.8	n.d.	14.4	n.d.	1.5	n.d.	5.5	n.d.	39.5	n.d.
31	n.d.	0.006	n.d.	2.3	n.d.	<0.01	n.d.	1.0	n.d.	9.5	n.d.	12.0
32	33.9	30.3	0.7	2.3	43.0	43.1	0.5	0.5	7.5	6.0	52.0	49.5
33	12.9	11.5	0.7	1.9	<0.01	14.8	0.5	1.0	8.5	13.5	24.0	74.0
34	0.098	14.3	2.3	1.9	<0.01	<0.01	1.0	1.0	12.5	4.5	27.0	29.5
35	19.0	14.2	2.1	2.5	15.7	13.4	1.0	0.5	12.0	8.0	73.0	42.0
36	<0.005	<0.005	0.8	2.2	<0.01	9.5	0.5	0.5	4.0	3.5	20.0	14.0
37	0.382	0.536	0.8	2.0	<0.01	13.1	0.5	0.5	4.5	5.0	39.0	26.5
38	<0.005	<0.005	1.1	2.7	<0.01	4.1	0.5	1.0	7.0	9.0	18.5	12.0
39	<0.005	<0.005	0.4	<0.01	32.6	30.6	1.0	1.0	8.0	7.5	13.0	10.0
40	<0.005	<0.005	0.3	1.9	40.9	28.1	0.5	0.0	31.5	31.0	17.0	8.5
41	<0.005	<0.005	0.9	2.5	<0.01	9.1	<0.1	<0.1	6.0	7.0	12.0	11.0
42	n.d.	0.637	n.d.	5.7	n.d.	<0.01	n.d.	2.5	n.d.	42.0	n.d.	80.5
43	n.d.	5.25	n.d.	<0.01	n.d.	<0.01	n.d.	0.5	n.d.	2.5	n.d.	25.0

Sample ID	Cr(VI) pre-m.	Cr(VI) m.	F^- pre-m.	F^- m.	NO_3^- pre-m.	NO_3^- m.	As pre-m.	As m.	Mo pre-m.	Mo m.	U pre-m.	U m.
	(mg L^{-1})						(µg L^{-1})					
Chhiwali												
44	<0.005	<0.005	8.2	2.3	<0.01	10.4	0.5	<0.1	7.0	8.0	14.0	17.0
45	78.3	115	1.2	2.7	137	123	0.5	<0.2	24.5	16.0	103	70.0
46	<0.005	<0.005	<0.01	<0.01	<0.01	76.9	1.0	2.0	43.5	76.0	77.0	62.5
47	<0.005	<0.005	<0.01	<0.01	138	160	1.5	1.5	21.5	24.5	140	127
48	0.002	0.014	6.9	9.2	224	224	2.0	2.0	15.5	17.0	168	140
49	n.d.	<0.005	n.d.	3.2	n.d.	<0.01	n.d.	1.5	n.d.	12.5	n.d.	22.0
50	0.023	0.023	14.2	<0.01	600	525	2.5	3.0	117	99.5	260	185
51	0.816	0.028	3.6	11.0	40.7	<0.01	9.5	10.5	90.0	105	146	210
52	<0.005	<0.005	3.5	3.9	<0.01	<0.01	1.5	1.5	42.0	43.0	33.0	19.5
53	0.174	0.669	9.5	33.1	233	154	1.0	3.5	38.5	97.0	290	350
54	0.011	0.011	2.2	23.3	361	214	3.5	3.5	160	43.0	330	183
55	0.012	0.038	11.8	2.0	264	157	4.0	4.0	92.0	83.5	308	236
56	<0.005	<0.005	1.6	3.3	15.1	14.9	<0.1	0.5	13.5	14.0	66.0	67.5
57	<0.005	<0.005	<0.00	<0.01	<0.01	<0.01	<0.1	<0.1	11.0	22.5	52.0	110
58	8.58	9.40	<0.01	<0.01	320	374	2.0	1.5	1.5	1.5	24.5	41.5
59	<0.005	<0.005	<0.01	<0.01	423	386	<0.1	0.5	2.5	2.5	31.5	40.5
60	0.005	0.348	<0.01	<0.01	4236	2995	2.5	7.0	18.0	106	52.0	67.0
61	<0.005	n.d.	1.7	n.d.	165	n.d.	74.5	n.d.	1900	n.d.	128	n.d.
62	n.d.	<0.005	n.d.	3.0	n.d.	20.1	n.d.	0.5	n.d.	14.0	n.d.	35.0
63	<0.005	0.069	<0.01	<0.01	4481	4470	2.0	2.0	116	56.0	47.5	36.0
64	<0.005	<0.005	8.2	2.3	<0.01	10.4	0.5	<0.1	7.0	8.0	14.0	17.0
65	78.3	115	1.2	2.7	137	123	0.5	<0.2	24.5	16.0	103	70.0
66	<0.005	<0.005	<0.01	<0.01	<0.01	76.9	1.0	2.0	43.5	76.0	77.0	62.5
67	<0.005	<0.005	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Sample ID	Cr(VI) pre-m.	Cr(VI) m.	F^- pre-m.	F^- m.	NO_3^- pre-m.	NO_3^- m.	As pre-m.	As m.	Mo pre-m.	Mo m.	U pre-m.	U m.
	(mg L^{-1})						(µg L^{-1})					
Godhrauli												
68	0.401	0.304	4.4	3.5	48.4	66.2	1.0	0.5	14.0	13.5	71.0	45.0
69	1.20	2.00	4.2	10.9	105	135	1.5	0.5	19.0	19.0	53.5	100
70	1.11	0.778	4.0	3.7	34.5	42.6	0.5	0.5	21.5	21.5	56.0	54.0
71	<0.005	<0.005	1.5	2.3	<0.01	<0.01	0.5	0.0	34.5	33.5	40.5	41.0
72	1.83	1.96	0.7	2.7	44.5	53.1	0.5	0.5	2.5	2.5	22.5	76.5
73	n.d.	<0.005	n.d.	2.6	n.d.	<0.01	n.d.	11.5	n.d.	3.5	n.d.	84.0
74	<0.005	<0.005	3.7	2.7	<0.01	<0.01	12.5	9.5	7.0	11.0	8.0	9.5
75	0.016	0.010	4.2	5.6	<0.01	<0.01	0.5	1.0	18.5	23.5	79.5	108

Table S4 Solute concentrations of the investigated wells in the study area. n.d., not determined; pre-m., pre-monsoon; m., monsoon.

Sample ID	Cl$^-$ pre-m.	Cl$^-$ m.	SO$_4^{2-}$ pre-m.	SO$_4^{2-}$ m.	Ca pre-m.	Ca m.	K pre-	K m.	Mg pre-m.	Mg m.	Na pre-m.	Na m.
	(mg L^{-1})						(mg L^{-1})					
Rania												
1	14.9	20.3	15.4	17.6	27.4	24.7	2.9	3.4	37.9	41.3	70.6	91.4
2	14.9	12.7	3.3	2.6	18.9	13.2	2.7	2.3	18.9	19.5	63.7	92.6
3	92.3	114	85.3	103	142	134	29.5	31.4	32.6	46.9	99.9	93.1
4	486	335	369	327	68.2	157	776	306	87.6	107.1	316	233
5	n.d.	36.3	n.d.	23.1	n.d.	38.6	n.d.	84.9	n.d.	22.1	n.d.	51.2
6	n.d.	305	n.d.	273	n.d.	137	n.d.	273	n.d.	82.3	n.d.	195
7	22.9	34.0	33.2	48.7	56.7	55.4	2.6	3.2	29.2	41.0	66.3	80.3
8	458	343	320	112	57.5	57.1	143	120	60.7	69.7	411	394
9	31.3	35.8	17.4	19.9	25.8	24.6	3.8	4.4	39.9	48.4	40.8	52.0
10	12.8	17.2	19.4	22.3	61.1	58.7	3.3	3.9	26.5	35.7	58.6	51.8
11	107	112	200	229	83.5	76.7	7.3	7.6	46.5	68.0	175	202
12	n.d.	90.6	n.d.	161	n.d.	91.2	n.d.	6.8	n.d.	65.0	n.d.	164
13	n.d.	92.3	n.d.	102	n.d.	59.7	n.d.	5.0	n.d.	49.7	n.d.	97.0
14	n.d.	61.5	n.d.	60.6	n.d.	47.2	n.d.	4.5	n.d.	35.1	n.d.	97.5
15	50.5	55.8	40.8	44.5	18.9	15.2	3.5	3.5	25.8	29.3	150	161
16	9.9	19.7	11.3	13.9	19.8	20.1	7.5	7.8	30.2	33.3	168	139
17	77.9	82.5	316	312	9.4	8.3	3.2	3.5	12.2	16.9	361	394
18	33.0	34.7	117	91.3	8.1	7.4	3.0	3.4	11.2	14.3	233	273
19	n.d.	154	n.d.	349	n.d.	116	n.d.	3.6	n.d.	53.1	n.d.	203
20	n.d.	15.8	n.d.	72.7	n.d.	53.5	n.d.	3.3	n.d.	34.9	n.d.	96.2

Sample ID	Cl$^-$ pre-m.	Cl$^-$ m.	SO$_4^{2-}$ pre-m.	SO$_4^{2-}$ m.	Ca pre-m.	Ca m.	K pre-	K m.	Mg pre-m.	Mg m.	Na pre-m.	Na m.
	(mg L^{-1})						(mg L^{-1})					
Rania												
21	n.d.	59.2	n.d.	43.6	n.d.	50.9	n.d.	5.0	n.d.	53.5	n.d.	103
22	n.d.	198	n.d.	83.7	n.d.	61.2	n.d.	3.7	n.d.	48.0	n.d.	250
23	n.d.	21.1	n.d.	110	n.d.	7.7	n.d.	2.9	n.d.	15.9	n.d.	365
24	109	n.d.	16.8	n.d.	81.4	n.d.	5.2	n.d.	27.9	n.d.	60.0	n.d.
25	n.d.	176	n.d.	89.5	n.d.	114	n.d.	3.2	n.d.	55.2	n.d.	92.2
26	10.1	11.5	8.2	8.3	5.5	4.9	2.3	2.0	10.0	12.2	181	209
27	138	36.5	115	40.7	50.2	46.4	25.9	5.8	45.6	43.0	252	91
28	17.1	19.3	36.8	42.9	62.8	57.3	3.4	3.9	29.3	34.1	52.3	70.4
29	52.1	55.7	46.7	46.2	44.1	41.4	3.5	4.6	39.0	48.5	80.6	86.2
30	81.7	n.d.	86.4	n.d.	47.2	n.d.	5.0	n.d.	49.4	n.d.	111	n.d.
31	n.d.	15.6	n.d.	13.1	n.d.	17.2	n.d.	3.7	n.d.	30.3	n.d.	89.3
32	227	212	146	159	118	112	5.8	5.9	70.3	93.3	128	144
33	82.7	104	63.9	106	60.5	52.1	5.8	4.9	47.6	61.3	81.3	142
34	54.3	185	80.6	106	21.7	86.9	5.1	5.5	30.2	71.9	130	117
35	226	194	116	109	81.3	73.5	8.9	7.8	71.3	88.1	102	103
36	24.9	28.4	31.2	36.3	25.6	23.6	3.4	4.1	35.2	57.1	79.0	94.8
37	55.5	66.4	39.9	46.0	61.3	56.7	4.9	4.5	45.5	56.8	58.9	81.7
38	13.9	16.1	18.6	20.7	24.2	18.6	3.3	3.0	24.7	28.8	67.2	86.4
39	62.0	64.8	40.4	42.6	73.8	69.4	19.7	10.4	28.9	39.9	60.1	88.7
40	85.2	72.2	59.4	56.9	78.6	58.5	30.5	35.2	31.7	41.8	78.8	89.0
41	18.6	19.4	14.2	12.0	35.7	32.7	4.3	3.5	34.5	41.5	52.6	53.2
42	n.d.	158	n.d.	302	n.d.	15.7	n.d.	3.0	n.d.	25.5	n.d.	427
43	n.d.	300	n.d.	122	n.d.	78.5	n.d.	7.5	n.d.	84.7	n.d.	162

Sample ID	Cl^- pre-m.	Cl^- m.	SO_4^{2-} pre-m.	SO_4^{2-} m.	Ca pre-m.	Ca m.	K pre-	K m.	Mg pre-m.	Mg m.	Na pre-m.	Na m.
	(mg L^{-1})						(mg L^{-1})					
Chhiwali												
44	102	104	175	179	26.4	23.0	2.3	2.2	19.7	24.7	229	274
45	144	135	170	224	117	115	8.5	9.1	76.6	121	86.0	119
46	605	255	1208	427	71.3	30.1	4.1	3.6	60.7	36.1	670	644
47	252	275	527	519	56.5	42.5	6.6	6.6	41.3	57.0	508	590
48	366	324	495	434	57.2	58.5	7.3	7.5	41.7	70.8	523	517
49	n.d.	109	n.d.	101	n.d.	8.8	n.d.	1.0	n.d.	14.5	n.d.	330
50	722	623	965	821	64.2	52.5	8.0	7.6	77.3	79.9	943	846
51	170	200	180	232	17.3	16.2	10.1	10.1	13.9	19.4	392	622
52	39.2	45.3	21.3	17.8	12.0	11.8	3.9	3.3	6.8	10.5	105	116
53	494	309	863	392	24.4	20.6	5.5	5.4	24.1	26.7	479	454
54	639	396	1132	698	46.0	34.3	12.6	9.4	49.7	45.7	991	529
55	393	339	528	592	51.9	46.0	8.1	7.7	50.2	54.8	477	616
56	83.8	97.8	17.7	20.7	50.3	43.8	6.8	6.4	34.3	42.9	99.6	128
57	203	399	70.9	151	65.6	74.6	10.1	9.6	49.2	86.2	127	405
58	184	224	139	203	101	92.8	4.9	5.6	109	124	99.8	190
59	192	176	234	213	108	94.5	36.3	32.8	75.9	94.1	136	138
60	1354	1112	1897	1601	270	234	2056	1841	403	427	475	388
61	790	n.d.	858	n.d.	16.5	n.d.	2162	n.d.	52.7	n.d.	256	n.d.
62	n.d.	118	n.d.	86.7	n.d.	58.0	n.d.	6.1	n.d.	49.0	n.d.	86.7
63	1616	1426	2301	2128	284	284	3290	1995	320	429	495	280
64	56.8	n.d.	27.6	n.d.	57.6	n.d.	7.8	n.d.	41.3	n.d.	108	n.d.
65	n.d.	45.0	n.d.	15.7	n.d.	52.7	n.d.	7.9	n.d.	51.7	n.d.	124
66	41.4	12.1	8.5	3.7	59.5	58.2	6.7	5.9	44.7	56.4	45.7	51.6
67	89.0	n.d.	146	n.d.	33.6	n.d.	10.4	n.d.	28.9	n.d.	178	n.d.

Sample ID	Cl^- pre-m.	Cl^- m.	SO_4^{2-} pre-m.	SO_4^{2-} m.	Ca pre-m.	Ca m.	K pre-	K m.	Mg pre-m.	Mg m.	Na pre-m.	Na m.
	(mg L^{-1})						(mg L^{-1})					
Godhrauli												
68	104	101	71.8	64.7	32.4	33.8	25.3	24.9	30.1	38.9	169	147
69	206	235	351	301	61.7	52.6	19.0	17.0	68.7	73.6	179	407
70	120	126	177	123	55.5	52.0	13.0	13.4	51.4	72.5	348	140
71	66.4	70.2	44.4	40.0	57.3	56.1	42.4	35.0	27.0	38.3	142	81.3
72	121	139	126	144	83.2	80.6	35.5	35.1	63.9	88.5	101	99.3
73	n.d.	123	n.d.	145	n.d.	70.6	n.d.	55.4	n.d.	72.8	n.d.	165
74	107	105	72.0	76.5	32.5	16.5	100	105	47.1	11.9	104	102
75	108	169	199.0	317	37.7	32.4	8.8	8.6	54.9	71.1	113	330

Table S5 Sampling details of open dug wells (ODWs) used in estimation of hydraulic gradient in the Rania region aquifer.

Sample ID	Coordinates relative to an ellipsoidal surface			ΔElevation[a]	Ground-level[b]	Water-level[c]	Location
	(m)			(m)			
1	404509.106	2922758.84	63.637	1.510	0.95	3.27	Rania north
5	405255.986	2919790.708	64.601	2.474	2.024	5.91	Khan Chandpur
9	405605.511	2921225.912	63.774	1.647	1.497	4.66	Prasidhpur[d]
Base-station	404390.734	2921185.52	62.127				

[a] relative to base station elevation (Z).

[b] wells contained constructed steps above the ground level; the Trimble R10 GPS measurements of elevation were adjusted to calculate elevation of the ground level, by decreasing the well step height from estimated ΔElevation.

[c] relative to ground level

[d] also sampled for water quality (location 27 in Table S2-S4); other two wells were not sampled for water quality

Table S6 Median and maximum solute concentrations in mg L^{-1} for groundwater parameters in pre-monsoon and monsoon seasons and number of wells with increasing and decreasing solute concentration during the monsoon season.[a]

		Median		Max		Number of wells[b]	
		pre - monsoon	monsoon	pre - monsoon	monsoon	increasing conc.	decreasing conc.
Cl^-	Rania	52.1	55.7	486	343	16	7
	Chhiwali	228	265	1616	1426	6	10
	Godhrauli	108	126	206	235	3	0
SO_4^{2-}	Rania	3.3	2.6	369	327	15	6
	Chhiwali	365	32	2301	2128	6	10
	Godhrauli	126	123	351	317	3	4
Ca	Rania	50.2	52.1	142	157	2	19
	Chhiwali	58.4	49.3	284	284	1	11
	Godhrauli	55.5	52.0	83.2	80.6	0	4
K	Rania	4.3	4.5	776	306	12	11
	Chhiwali	7.7	7.6	3290	1995	2	8
	Godhrauli	25.3	24.9	100	105	0	2
Mg	Rania	32.6	41.8	87.6	107	25	0
	Chhiwali	49.5	56.7	403	409	14	2
	Godhrauli	51.4	71.1	68.7	88.5	5	2
Na	Rania	81.3	93.1	411	394	18	6
	Chhiwali	434	397	991	846	10	5
	Godhrauli	142	140	348	407	2	3

[a] only the wells investigated in both seasons were considered

[b] only wells with a change in element concentration > 5% were considered

Chapter 8 Comprehensive discussion

General discussion

To conclude how Cr contamination is associated with COPR in the area of Kanpur, *Chapter 8* provides a synthesis of the results, discussing the research hypotheses formulated in *Chapter 1* (outline of this thesis) with special regards to waste management strategies, followed by future prospects.

> ***Hypothesis 1*** ***– The COPR material from the Indian sites differs in its mineralogy and Cr content from COPR material obtained from Europe and the USA.***

The first hypothesis was based on the assumption that the Indian COPR material would differ in its mineralogy and Cr content due to differences in chromite ore composition, extraction process, deposition practice, outstanding weathering conditions, and the length of time spent in the landfill. The mineral phases, which were qualitatively identified in the two investigated Indian COPR samples were aragonite, brownmillerite, brucite, calcite, CAC-14, ettringite, magnesiochromite, grimaldiite, katoite, larnite, periclase, portlandite, quartz, sjogrenite, Na_2CrO_4, and voltaite. Except for grimaldiite and voltaite, these minerals had been identified previously in other COPR samples (Chrysochoou and Dermatas, 2007; Chrysochoou et al., 2010; Hillier et al., 2003). Grimaldiite, a chromium oxide-hydroxide [CrO(OH)], was identified in COPR for the first time. It was detected in both samples by XRPD, though identification based just on the reflex position was not easy. However, EDX analyses also indicated the presence of grimaldiite in the Chhiwali COPR sample. The second mineral, voltaite, was identified by XRPD, but the two reflexes had a relatively low intensity. Thus, and because identification by other methods failed, the presence of this mineral must be verified by future investigations. The origin of both minerals in the Indian COPR has not yet been clarified. Another difference from COPR material obtained from Europe and the USA is the use of ore originating from different locations, which varies in its composition. According to Tathavadkar et al. (2004), the composition of chromite minerals varies greatly depending on the conditions under which they were formed, e.g. magma composition, oxygen partial pressure and temperature during crystallization of magma, respectively. Hence, the origin of the ore is substantial for its composition. In general, the formulae of chromite range from ferrochromite ($FeCr_2O_4$), via $(Mg,Fe)Cr_2O_4$ to magnesiochromite ($MgCr_2O_4$). The ore used in the roasting process at Rania and Chhiwali was obtained from the Sukinda Valley (Jajpur district, Orissa, India). Chakraborty and Chakraborty (1984) investigated 17 chromite ore samples from the Sukinda Valley, as well as other parts of Orissa, and found Cr contents ranging from 332 to 418 g kg^{-1}, with a dominance of Mg in the spinel structure. This confirms the assumption that the residual ore found in the Indian COPR is predominantly magnesiochromite, which was identified by XRPD. Magnesiochromite was also used in the roasting process in Glasgow (Hillier et al., 2003); however, the ore used in the roasting process in New Jersey was at least partially ferrochromite (Burke et al., 1991). Apart from the type of ore, the content of the gangue materials, such as silicates, is important for the success of the roasting process (Antony et al., 2001). During roasting, Na_2CO_3 also reacts with silica, alumina, and iron bearing minerals, and forming sodium silicate, sodium aluminate, sodium ferrite, or complex iron-alumino-silicates (Tathavadkar et al., 2004). The sodium compounds formed could either interfere or enhance the formation of Na_2CrO_4 during the roasting (Tathavadkar et al., 2004). Thus, the origin of the ore significantly influences the success of the roasting process in a direct way (Tathavadkar et al., 2001, 2003) and indirectly impacts the content of the remaining Cr(III) in the COPR. Another important point is that the BCS works in Chhiwali do not actually have temperature controls for the roasting process. However, the extraction of Cr from chromite ore is dependent on roasting temperature and time (Tathavadkar et al., 2001). Tathavadkar et al. (2001) showed that the extraction of Cr from chromite ore increases as the roasting time and temperature rises. The roasting process in Chhiwali takes place at an estimated 1,100 °C and a roasting time of 45 min, although maximal Cr extraction is only achieved at 1,200 °C and a roasting time of 120 min (Tathavadkar et al., 2001), with the reaction rate decreasing after 60 min (Antony et al., 2001). However, Tathavadkar et al. (2001) and Antony et al. (2001) investigated the reaction parameters of the roasting process without the addition of lime. Altogether, the inefficiency of the roasting process was reflected in the high Cr content, 81.2 and 73.5 g kg^{-1}, of the COPR in this study, of which 20 and 13% was Cr(VI) respectively. Considering that the Cr content of the original ore was around 330 to 390 g kg^{-1} (data not published), the extraction rate is around 80%. However, the main problem is that Cr(III) is not completely oxidized to Cr(VI) in the soda-ash roasting process, which is reflected in the maximum extraction rates of 80-90% (Antony et al., 2006). Overall, the Cr and Cr(VI) contents of the investigated COPR were higher than reported for COPR in Europe (Cr: 10 to 70 g kg^{-1}, Farmer et al., 2006; Geelhoed et al., 2002; 2003; Hillier et al., 2003) and the USA (Cr: 13 to 70 g kg^{-1}, Burke et al., 1991; Chrysochoou et al., 2009a; Chrysochoou et al., 2010). However, it must be taken into consideration that only two Indian COPR samples were investigated and so a general conclusion is hard to obtain. Nevertheless, Földi et al. (2013) investigated six COPR samples in the area of Kanpur and found Cr values ranging from 65 to 109 g kg^{-1}, of which five samples exhibited Cr contents higher than 84 g kg^{-1}, supporting the assumption that the COPR found in this area contains a higher Cr content. It is likely that the young age of the Indian COPR, and thus the shorter weathering time is the main reason for the higher Cr(VI) content. Furthermore, leaching of Cr from the Indian COPR is diminished due to the short and low monsoonal precipitation compared to Glasgow and New Jersey, which have a higher annual precipitation (> 1000 mm) and no dry season. Another difference is the presence of easily soluble compounds, such as Na_2CrO_4 and sodium sulfate (Na_2SO_4), in the Indian COPR that have not been detected in other COPR materials. They were found in the pores of the Chhiwali COPR, where they are protected from leaching. Only the moderately soluble calcium chromate ($CaCrO_4$) has been previously detected in some COPR materials (Burke et al., 1991; Chrysochoou et al., 2009b) or in COPR-contaminated soils (James, 1994). The absence of such phases in the COPR material found in Europe and the USA may also be attributed to the higher age of these materials and the prevailing weathering conditions, as it is likely that the easily soluble phases were already leached out.

➔ ***Despite numerous similarities between the various COPR materials, mineralogical and chemical analyses revealed differences in element composition and Cr contents as well as the presence of phases that have not been previously detected in COPR, verifying Hypothesis 1.***

Summarized, highly alkaline COPR materials, with a high Cr content, are produced in the BCS works located in Chhiwali, via a high lime roasting process, and are still landfilled in the surroundings. To reduce the landfill of COPR in the future and to reduce the health risks for the local population, the processing of the chromite ore has to be improved. Various processes, such as acid leaching (Geveci et al., 2002; Zhao et al., 2014), alkali leaching (Chen et al., 2014a; Chen et al., 2014b; Zhang et al., 2010), and alkali fusion (Hundley et al., 1985), have been developed as alternative methods for processing chromite ore. However, soda-ash roasting, with or without the addition of lime, has been established on a commercial scale due to economic and technical reasons (Pariremyatwa et al., 2015). The use of alkali roasting to extract Na_2CrO_4, without the incorporation of lime, could be establish in the BCS works as a means of overcoming the formation of the highly toxic $CaCrO_4$ and to reduce the alkalinity that makes the treatment of COPR difficult. For the lime-free roasting process, conversion efficiencies of 85% have been reported for South African chromite ore (Tathavadkar et al., 2003). However, high-grade chromite ore with a silica content < 1% is necessary for the lime-free roasting process (Tathavadkar et al., 2003). Antony et al. (2006) investigated the lime-free alkali roasting of Indian chromite ores and concluded that the process can be used successfully for roasting Indian ores, although the conversion efficiency was limited to a maximum of 60 to 65% depending on the ore composition. Whether or not a non-lime roasting process is suitable for the Cr works in the area of Kanpur has to be carefully evaluated due to the composition of the ore. Chromite ore from the Sukinda valley in Orissa, investigated by Chakraborty and Chakraborty (1984), contains < 1% silica and is thus suitable for a lime free roasting process. However, investigations of the silica content of the chromite ore used in the Cr works in

Chhiwali (data not shown) showed 2.6 to 6.4% silica. Due to the high Cr contents of the investigated COPR, the recovery of Cr as Na_2CrO_4 from the COPR via pyrometallurgical or hydrometallurgical processes may also be a possible way of reducing the Cr content in the waste (Antony et al., 2001). Antony et al. (2001) investigated these issues and achieved a maximum recovery of Cr from the COPR of 83%. Antony et al. (2006) reported that COPR can also be used as a replacement for lime to efficiently maintain conditions during non-lime alkali roasting. Industrial symbiosis may also be another possibility for recycling deposited COPR material. Chromite ore processing residue can be used as a replacement for limestone or dolomite as an alkaline flux, especially in the sintering and iron-making industry (Wu et al., 2015). The young age of the deposited Indian COPR, may for that reason, be helpful, as it has kept its chemical activity. Wu et al. (2015) reported that the reduction efficiency of Cr(VI) was 98.4%. In the Kanpur area, some iron-making and steel-making industries that could benefit from the COPR material occurs.

If the COPR is not removed from the dumpsites, the high amounts of Cr(VI) will constitute an enduring danger to human health due to the inhalation of airborne particles or the contamination of surface and groundwater. To evaluate the risk arising from COPR dumps, Cr(VI) leaching behavior was investigated using column experiments under water-saturated conditions. As differences in the mineralogical and chemical composition of the Indian COPR were found, the following hypothesis was developed:

> ***Hypothesis 2*** ***– Mineralogical composition significantly influences the leaching of Cr(VI) from COPR.***

Of the mineral phases mentioned before, Na_2CrO_4, CAC-14, and katoite were found to control the release of Cr(VI). The leached Cr(VI) concentrations decreased from 1800 to 300 mg L^{-1} (Rania site) and 1200 to 163 mg L^{-1} (Chhiwali site) during 12 pore volumes, which conforms to 2 year of monsoon precipitation. These values exceeded the guideline value of 0.05 mg L^{-1} set up both by the World Health Organization (WHO, 2011) as well as the Bureau of Indian Standards (BIS, 2009) by an order of magnitude of 4 to 5. In previous studies CAC-14 and katoite were found to control the release of Cr(VI) at pH values above 11 (Geelhoed et al., 2002; Wazne et al., 2008). However, the release of Cr(VI) from the Indian COPR could not be described by considering just these two mineral phases as these phases are stable down to a pH value of 11 (Chrysochoou et al., 2009a), which was not achieved in the column experiment. The results of this study support the assumption that the release of Cr(VI) is dominated by highly soluble phases, such as Na_2CrO_4, which are present in Indian COPR but not in COPR obtained from the Glasgow and New Jersey site. Furthermore, the release of Cr(VI) was partially rate limited, although this was more obvious in the Rania COPR. Rate limited release of Cr(VI) could be attributed either to the slow dissolution kinetic of some Cr(VI) phases, such as

$CaCrO_4$ (James, 1994), or the diffusion of Cr(VI) from the inside of particles to the solution (Higgins et al., 1998). The latter may be important, as, for instance, Na_2CrO_4 was found in pores protected from leaching. The fact that the pH only slightly decreased, from 12.3 to 11.7 (Rania site) and 12.6 to 12.1 (Chhiwali site), due to the presence of portlandite and carbonate phases implies a high buffer capacity, which is important as the dissolution of mineral phases is heavily dependent on pH. Therefore, it could be expected that pH will not significantly change over the next decades.

- ➔ ***Slightly soluble phases and the high buffer capacity significantly influence the leaching of Cr(VI) from the Indian COPR and thus verifying Hypothesis 2.***

A decrease in the solid-phase Cr(VI)/Cr_{total} ratio after the column experiment revealed that it was almost exclusively Cr(VI) that was leached. Furthermore, the leaching of Cr(VI) was highest in the inflow section of the column and approximately zero in the outflow section. In total, only 16% of the total Cr(VI) was leached. Considering that the experiment was performed in a 20 cm column, while the COPR heaps on site are several meters thick, it can be concluded leaching of Cr(VI) at these sites will be ongoing for an indefinite period of time if the source of the Cr(VI) is not removed or remediation is not initiated. This is also confirmed by the fact that the COPR materials in Glasgow and New Jersey, which are much older compared to the Indian COPR, are still leaching Cr(VI) in concentrations of up to 91 (Farmer et al., 2002) and 30 mg L^{-1} (Burke et al., 1991).

Several studies have been conducted to investigate the treatment of COPR. In general, remediation can be performed either ex situ or in situ. In terms of ex situ remediation, thermal treatment of COPR has been investigated (Wang et al., 2007; Zhang et al., 2009a; Zhang et al., 2009b; Zhang et al., 2009c). Thermal treatment can be achieved via pyrolysis, i.e. the burning in the presence of organic carbon as a reductant for Cr(VI). However, ex situ remediation is linked with significantly higher costs and this approach is difficult to implement in this area. Furthermore, the COPR dumps in Rania, Chhiwali, and Godhrauli are located close to inhabited and agricultural areas; therefore an ex situ approach could increase the potential risk of human exposure to Cr(VI) by inhalation of fine particles via the airborne dispersion route. In situ remediation is mainly based on the chemical reduction of Cr(VI) to the less harmful Cr(III) species. Geelhoed et al. (2003) investigated the effect of Fe(II)SO_4 and $FeCl_2$ addition on Cr(VI) leaching in soil columns and concluded that Fe(II) was not effective for the remediation of Cr(VI) in COPR due to the high pH, which causes Fe(II) to precipitate. Wazne et al. (2007b) also reported that pH adjustment is necessary for effective treatment with Fe(II)SO_4. Additionally, Cr(VI) is released from COPR through an anion exchange with sulfate for CrO_4^{2-} (Geelhoed et al., 2003). The reduction and immobilization of Cr(VI) in COPR was also investigated using nano-zero valent iron (Cao and Zhang, 2006; Du et al., 2012). The results indicated that despite a relatively high reduction rate, this remediation approach is only applicable for groundwater or COPR-slurry with small particle size. However, Watts et al. (2015) demonstrated the applicability of nano-magnetite and nano-zero valent iron treatments in situ, with no pre-addition acidification of the COPR needed. Some studies have identified calcium polysulfide (CaS_5) as effective for the remediation of COPR (Graham et al., 2006; Moon et al., 2008; Wazne et al., 2007a; Wazne et al., 2007b). Thereby, CaS_5 acts as a reductant for Cr(VI), which is reduced to Cr(III) followed by precipitation as $Cr(OH)_3$. Dong et al. (2011) and Hsu et al. (2009) identified biochar as an effective means of removing of Cr(VI) from soils and aqueous solutions. However, there are no studies available dealing with the use of biochar for the remediation of COPR. The main aim of the aforementioned remediation strategies is to reduce the slow and continuous release of Cr(VI) from COPR, as described in *Chapter 4*. Much of the Cr(VI) was not released from the solids and is therefore not accessible to reductants. As Cr(VI) is only stepwise released over time, the availability of the reductant decreases (e.g. due to leaching or re-oxidation). In this case, the stepwise addition of a reductant is required and a long curing time is necessary. Thus, as pretreatments of the COPR (e.g. acidification) are partially necessary, the cost of this potential treatment rises.

Due to the specific chemical composition of the COPR leachates, in particular their high pH, which is known to influence anion adsorption in soils, the following hypothesis was formulated.

> ***Hypothesis 3*** ***– COPR leachate composition influences the*** **CrO_4^{2-} adsorption behavior of soils.**

To validate this hypothesis, batch experiments with COPR eluates and three uncontaminated soils were carried out. The results showed that the quantity of CrO_4^{2-} adsorbed by the soils (pH = 6.7 to 7.2) was very low for both eluates and decreased with increasing soil pH and decreasing content of pedogenic Fe oxides. This fact was also reflected in low Freundlich constants, ranging from 0.20 to 7.25 μmol^{1-n} kg^{-1} L^n (Rania COPR eluate) and 0.50 to 2.46 μmol^{1-n} kg^{-1} L^n (Chhiwali COPR eluate). In general, CrO_4^{2-} adsorption is inhibited at neutral to alkaline pH values (Ajouyed et al., 2010; Jiang et al., 2008), as was the case in our experiment. Whether or not ionic strength, which was very high in the COPR eluates, influences CrO_4^{2-} adsorption is controversial (Ajouyed et al., 2010; Mesuere and Fish, 1992a); however, more important is which ions dominate in the solution. Sulfate was also present in concentrations of up to 0.17 mmol L^{-1} in the COPR eluates and may compete for binding sites. Villalobos et al. (2001) and van Geen et al. (1994) reported that high concentrations of carbonate (CO_3^{2-}) might also negatively affect CrO_4^{2-} adsorption. In this study CO_3^{2-} was not measured in the COPR eluates or in the COPR leachates; however, Geelhoed et al. (2002) found CO_3^{2-} concentrations of up to 0.27 mmol L^{-1} in COPR eluates. Considering that the batch experiments were carried out with Cr(VI) concentrations ranging from 0.07 to 6.77 mmol L^{-1} for the Rania COPR and 0.05 to 5.12 mmol L^{-1} for the Chhiwali COPR, the effect of competing anions is only intermediate. Altogether, the investigated soils only had a low maximum CrO_4^{2-} adsorption capacity (S_{max}) ranging from 0.40 to 0.47 mmol kg^{-1} (Rania COPR eluate) and 0.33 to 0.44 mmol kg^{-1} (Chhiwali COPR eluate), under these experimental conditions. Considering that in the column experiment Cr(VI) concentrations of 34.6 to 5.8 mmol L^{-1} (Rania site) and 23.1 to 3.1 mmol L^{-1} (Chhiwali site) were leached, a high discharge of Cr(VI) from COPR into the groundwater is expected. Furthermore, it should be noted that the batch experiments were carried out at the pH of the soils (the best case scenario) and not at the alkaline pH of the COPR-eluates (the worst case scenario). However, the results of the column study indicated that the COPR leachates have a high buffer capacity. Thus, it is likely that a change of pH in the percolating solution from very alkaline to the soil pH will not occur as long as the soils have a neutral pH value, which was the case in this study.

- ➔ ***It can be concluded that mainly the high pH of the COPR leachates influences CrO_4^{2-} adsorption, verifying Hypothesis 3. The influence of competing anions present in the leachates is limited and has a modifying effect at most.***

Since the results of the batch experiments showed that CrO_4^{2-} from the COPR leachates is retarded to a certain amount in soils, the question arose, in which geochemical fraction is it predominantly present. Therefore, Cr was fractionated sequentially in a soil contaminated by COPR leachates. The results indicated that Cr was associated predominantly with short-range-ordered (42.9%) and crystallized Fe (hydr)oxides (27.1%), followed by the residual fraction (18.7%). Chromate adsorption by organic compounds and Mn oxides was negligible (together about 2.5%). The high Cr concentration related to the mobile (4.6%) and exchangeable (4.2%) fraction was noticeable, of which most was Cr(VI). The high percentages of mobile and exchangeable Cr in the soils resulted from Cr(VI) intake caused by the COPR leachates. This is alarming, as the soil is used for agriculture (e.g. rice cultivation). Furthermore, when this soil is inundated, for instance during water saturation after monsoon rains or flood irrigation, the redox potential (E_H) is expected to change from oxidizing to reducing conditions, which may affect the speciation and dynamics of the Cr in the soil. Thus, *Hypothesis 4* was formulated.

Hypothesis 4* – *Cr(VI) release from COPR-contaminated soil is influenced by varying water content and redox conditions.

To validate this hypothesis, the soil was packed into columns and subjected to saturation-drainage-saturation cycles. In general, E_H decreased slowly at the beginning of the experiments and reached a minimum of −100 mV after 70 d. As mentioned above, high Cr(VI) concentrations were present in the mobile fraction that controlled the E_H by $CrO_4^{2-}/Cr_2O_3(s)$, or

CrO_4^{2-}/(Fe,Cr)OOH redox couples. Since the standard electrode potential of CrO_4^{2-}/Cr(III) is high ($E^0 = 1.51$ mV), the electrons in the soil solution scavenge using Cr, preventing the E_H from decreasing. The results showed that Cr(VI) was mobile under oxidizing conditions and gradually immobilized and irreversibly sequestered via reductive precipitation under reducing soil conditions. A maximum Cr(VI) concentration of 200 mg L^{-1} was achieved in the pore water at the beginning of the experiment, which exceeds the guideline value by a factor of 4,000. After soil drainage and a return to oxidizing conditions, only small amounts were remobilized, resulting in a maximum Cr(VI) concentration of 5 mg L^{-1}. Considering that the E_H in the COPR contaminated soil only decreased slowly, a high discharge of Cr(VI) into the groundwater is expected.

➔ ***Based on the results it can be concluded that Cr(VI) release from a COPR-contaminated soil is influenced by varying water content and redox conditions and thus Hypothesis 4 is verified. On the other hand, the E_H itself is influenced by high Cr(VI) concentrations in the pore water.***

With respect to the use of this soil as cultivation area, the potential uptake of Cr(VI) by plants is of particular interest. Xiao et al. (2013) established a model for evaluating the phytoavailability of Cr to rice in six representative Chinese soils relative to soil properties. Based on the maximum safe level of daily Cr intake, the authors found values ranging from 0.56 to 2.18 mg kg^{-1} for Mehrlich–3 extractable Cr. These values are distinctly lower compared to the exchangeable Cr content of the COPR-contaminated soil, which was 47.4 mg kg^{-1}. However, at comparison of the values obtained from the Mehrlich−3 extraction (0.2 mol L^{-1} CH_3COOH, 0.25 mol L^{-1} NH_4NO_3, 0.015 mol L^{-1} NH_4F, 0.013 mol L^{-1} HNO_3, 0.001 mol L^{-1} EDTA) and the extraction according to Zeien and Brümmer (1989) (1 mol L^{-1} NH_4OAc at pH 6) is limited by the different extraction reagents used. Despite the limited comparability, it is evident that the rice cultivated in the COPR-contaminated soil may not be suitable for human consumption. However, as described above, Cr(VI) concentrations decrease under reducing conditions, which may be beneficial with respect to wet rice cultivation. Xiao et al. (2015) investigated the effect of irrigation management on the dynamics of pore water Cr(VI) concentration in rice paddies, as well as the Cr distribution in rice. The authors concluded that continuous flooding is better than alternating wet and dry conditions, as Cr(VI) concentrations decreased over time after planting, resulting in a lower Cr(VI) content in the rice tissues. However, E_H values of −200 to −250 mV were achieved within 30 d in the experiments of Xiao et al. (2015), which is much faster than in the COPR-contaminated soil. Thus, it is doubtful if the rice cultivated in the COPR-contaminated soil is edible, even if the soil is permanently flooded. It has been previously shown that high amounts of Cr(VI) are leached out from COPR dumps and the adsorption capacity of surrounding soils is assumed to be low. Since it has been proved that COPR dumps are the source of groundwater contamination, the following hypothesis was developed.

> ***Hypothesis 5*** ***– Groundwater is highly contaminated with Cr(VI) in the surroundings of the COPR dumpsites.***

To investigate this issue, it was necessary to identify the spatial distribution of the COPR dumpsites in the study area. In Rania five COPR dumpsites were found, with the largest covering an area of around 55,800 m^2 and containing heaps varying between 0.5 and 1.5 m. Furthermore, the closed BCS manufacturing unit, which is located opposite the main dumping site, also hosts huge quantities of COPR. Chromite ore processing residue was also used as a grounding material for road construction in Rania. The dumpsites at Chhiwali (seven in total) and Godhauli (five in total) were smaller, covering a maximum area of 8,100 m^2 (Chhiwali) and 5,200 m^2 (Godhrauli) respectively.

The analyses of 75 wells indicated groundwater contamination with Cr(VI), F^-, NO_3^-, As, Mo, and U. In total, 95% of the wells exceeded the international threshold values and thus did not provide safe drinking water. Furthermore, most samples exhibited multiple contaminates from various elements. While the contamination of F^-, As, Mo, and U was considered to be geogenic, elevated Cr(VI) values were related to the COPR dumps. In a further risk assessment of the COPR dumps, the wells were classified according to their total Cr concentration. The results showed that in total 20% of the wells were moderately ($0.05 \text{ mg L}^{-1} < \text{Cr} < 1 \text{ mg L}^{-1}$) and 21% highly ($\text{Cr} > 1 \text{ mg L}^{-1}$) contaminated. In Rania, the highest Cr(VI) concentrations were found close to the main COPR dumping site (23 mg L^{-1}), northward along the street in Umran (35 mg L^{-1}), and also in the village of Khan Chandpur (30 mg L^{-1}), which is approximately 2 km south of the main dumping site. The high Cr(VI) values in the wells at Khan Chandpur were not related to the COPR dumps in the direct vicinity, but rather to a Cr(VI) plume spreading in a south to south-easterly direction from the main dumpsite. On the other hand, there were also wells with uncontaminated water within less than 300 m of the main COPR dumpsite. In Chhiwali, the maximum Cr(VI) concentration of 115 mg L^{-1} was detected in a well adjacent to the COPR dumpsite. However, there were several wells directly adjacent to COPR dumpsites that were not contaminated with Cr(VI). A similar spatial Cr(VI) distribution was observed in Godhrauli, with maximum Cr(VI) concentrations (2.0 mg L^{-1}) being lower than in the other two locations.

➔ ***Hypothesis 5 was only partially confirmed. Despite the presence of Cr(VI) contaminated water within a certain range of the COPR dumpsites, there were also wells adjacent to the dumpsites that were uncontaminated. Furthermore, in one case, a plume with elevated Cr(VI) concentrations was identified some distance away from the COPR dumpsites.***

Since the leaching of Cr(VI) from COPR is directly linked to the incidence of seepage water, and the local population reported that the color of the well water changes from colorless to yellowish during the monsoon season the following hypothesis was constructed.

> ***<u>Hypothesis 6</u> – Monsoon precipitation drives the influx of Cr(VI) from the COPR dumpsites into the groundwater resulting in elevated Cr(VI) concentrations.***

To investigate these issues, groundwater samples were taken during the pre-monsoon (n = 57) and monsoon (n = 70) seasons. The results showed that Cr(VI) concentrations increased in some wells during the monsoon season (n = 11), while in other they decreased (n = 10). Furthermore, median values were relatively unaffected by sampling season. This was also supported by the results of a t-test, which revealed no significant differences between the pre-monsoon and monsoon periods in terms of groundwater contamination by Cr(VI).

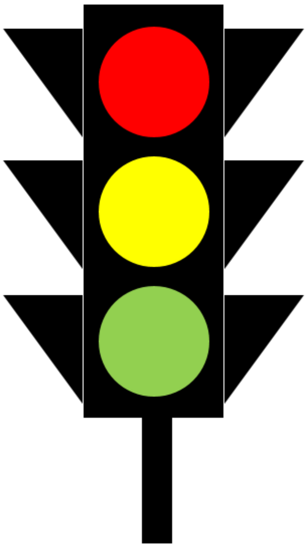
➔ ***It could not be confirmed that monsoon precipitation leads to elevated Cr(VI) groundwater concentrations, thus Hypothesis 6 is not supported.***

There may be many reasons for this. On the one hand, the seasonal rainfall in the sampling year was 42% less than the long-term average. On the other hand, the time scale of the infiltration and onward transportation to the sampled locations may be longer than the two-month monsoonal period considered in this study. Thus, the measured Cr(VI) values are rather the result of other factors including (i) diurnal variations, (ii) irrigation effects, and (iii) the replacement of water in open dug wells. Diurnal variations seem to be dependent on water consumption by the households and irrigation. Some villagers reported that the water is apparently clean in the morning and turns yellowish in the evening. This was also observed in the water from open dug wells, which was initially clean but which became contaminated within weeks. Altogether, there is probably hydraulic windows that exist between the different groundwater stories, e.g. where well drilling was inappropriate. For a further risk assessment, it is necessary to establish monitoring programs not only for Cr(VI) but also for the other elements in the affected areas.

Regarding the overall situation of the investigated area in terms of the occurrence of COPR dumpsites, the associated leaching of Cr(VI), and the distribution of Cr(VI) in the groundwater, the following considerations arose:

Farmer et al. (2006) reported that the capping of COPR dumpsites is recommended at least as a short- to medium-term measure, which is already in practice at most of the COPR-impacted sites in the Glasgow area. This could also be a possibility for the COPR sites investigated in this study. Capping minimizes the potential for Cr(VI) leaching from COPR; however, it provides no solution for dealing with the groundwater that is already contaminated (Farmer et al., 2006); therefore, the remediation of contaminated groundwater is necessary. The remediation of Cr(VI) contaminated water and wastewater has been intensively studied (Farmer et al., 2006; Owlad et al., 2009) and ensued in a conventional pump and treat (P&T) system, via an in-situ reduction system, or by migration through a permeable reactive barrier. In a P&T setup, the contaminated water is pumped out of the aquifer, treated on the surface, and then returned to the aquifer (Voudrias, 2001). An advantage of the P&T setup is that established treatment techniques can be used, e.g. adsorption techniques (activated carbon, biosorbents, industrial waste sorbents, chitosan), membrane filtration techniques (inorganic, polymeric, liquid membrane), anion exchange techniques, or electrochemical treatment techniques (Owlad et al., 2009). However, P&T technologies are time-consuming and costly, particularly when the contaminated water is widespread. Since in Rania, Chhiwali, and Godhrauli several aquifers are contaminated and the Cr(VI) contamination varies on a small scale, P&T technologies are not useful in these area. An in-situ remediation by injection of reductants, such as a blend of $Na_2S_2O_4$ and $FeSO_4$ into the contaminated water, has been suggested (Ludwig et al., 2008; Su and Ludwig, 2005). However, if the source of the contamination is not removed, multiple injections of the reductant are required. This problem could be overcome by Cr(VI) reduction using a permeable reactive barrier. In this context, permeable reactive barriers impregnated with zero-valent iron or FeS_2 have been shown to be effective (Astrup et al., 2000; Blowes et al., 1997). McLeod (2001) investigated the potential usefulness of pillared modified clay for simultaneously absorbing Cr(III) and Cr(VI) and recommended it as a treatment media in permeable reactive barriers. Another option is the incorporation of biological reductants into a permeable reactive barrier. A number of aerobic and anaerobic microorganisms are considered capable of reducing Cr(VI) to Cr(III) (Barrera-Diaz et al., 2012; Cheung and Gu, 2007; Narayani and Shetty, 2013). The main mechanisms of Cr(VI) reduction are related to the catalysis by enzymes or membrane-associated reductases (Cheung and Gu, 2007).

Even if groundwater remediation at the dumpsites is initiated immediately, the local population will still suffer from contaminated water for years. Therefore, an awareness campaign among the villagers is essential to inform them about the dangers of consuming Cr(VI) contaminated water. In this context, it would be helpful to color the existing wells according to the traffic light color system:



- Cr > 1 mg L^{-1}
- Water is toxic and not utilizable.

- 0.05 mg L^{-1} < Cr < 1 mg L^{-1}
- Water is only useful to a limited extent.

- Cr < 0.05 mg L^{-1}
- Water is safe and suitable for drinking and cooking.

Since the results of the groundwater investigations showed that Cr(VI) concentrations may change, water safe samples should be checked regularly for Cr. For the villagers who do not have any access to uncontaminated water, a Cr elimination method that can be employed at the level of individual households to produce drinking water should be developed and established. Given the low income and poor education of the rural population, a robust and simplistic method that is accepted by the local population is essential. Some success with the treatment of COPR contaminated water has been achieved using $FeSO_4$ (Hursthouse, 2001; Su and Ludwig, 2005). In this case, Cr(VI) is chemically reduced to Cr(III) by the ferrous ion and subsequently precipitated as a mixed Fe(III)/Cr(III) hydroxide. Compared to other treatment options, reduction by $FeSO_4$ is rapid (Hursthouse, 2001) with the simultaneous precipitation of Cr(III), which reduces the total dissolved Cr concentration to below the drinking water guidelines (Su and Ludwig, 2005). The advantage of this method is that no analytical equipment is required and the chemicals are simple and cheap to obtain. However, before this treatment method is applied in the villages, Cr(VI) elimination rates, chemical dosage, and filter handling should be investigated. After this, the method could be spread by training the villagers and with the participation of the head villager. Furthermore, a successful implementation must include ongoing quality control.

Future prospects

This thesis should be considered as basic research of the Cr contamination associated with COPR in the area of Kanpur. Hence, further research should be undertaken to counteract the negative effects of the Cr(VI) associated with this waste. Thus, the following aspects should be taken into consideration:

- The selection of remediation approaches for COPR-contaminated sites is difficult, as it depends to a large extend upon site-specific conditions. Further research in this field should be undertaken.
- In this study, only two COPR samples from different locations were investigated in detail. However, COPR is known to be a heterogeneous material; therefore, conclusive statements are hard to give. As a result, numerous samples should be analyzed in detail in terms of their chemical and mineralogical composition. After this, selected samples could be used for further leaching studies.
- The mineralogical data presented in this study is based on qualitative investigations; however, quantification of the mineral phases are required for a process-based modeling framework and further risk assessment.
- Although the high lime roasting process has been intensively studied, no quantitative information about the chemistry and mineralogy of the phases that emerge from each production step is available. Hence, samples of the raw ore, material after roasting, and the freshly produced COPR material after leaching should be taken and further investigated.

  Similarly, only limited information about the weathering of COPR material on site is available. Thus, it is of particular interest to study the weathering of COPR (e.g. carbonation). It would also be helpful to investigate single COPR heaps in layers from the crust to the core in order to obtain information about weathering in relation to climate conditions.

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Paper contributions

1. **Matern, K.**, Kletti, H., Mansfeldt, T. Chemical and mineralogical characterization of chromite ore processing residue from two recent Indian disposal sites. *Chemosphere (2016) 155:188-195.*
   Erhebung der Daten im Labor: 85%
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2. **Matern, K.**, Weigand, H., Kretzschmar, R., Mansfeldt, T. Leaching of hexavalent chromium from young chromite ore processing residue. *Manuscript.*
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3. **Matern, K.**, Mansfeldt, T. 2016. Chromate adsorption from chromite ore processing residue eluates by three Indian soils. *Environmental Chemistry (2016) 13:674-681*.
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   Verfassen der Publikation: 95%

4. **Matern, K.**, Mansfeldt, T. Chromium release from a COPR-contaminated soil at varying water content and redox conditions. *Journal of Environmental Quality (2016) 45:1259-1267.*
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   Verfassen der Publikation: 95%

5. **Matern, K.**, Weigand, H., Singh, A., Mansfeldt, T. Environmental status of groundwater affected by chromite ore processing residue (COPR) dumpsites during pre-monsoon and monsoon seasons. *Environmental Science and Pollution Research (in press). doi:10.1007/s11356-016-8110-2*
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   Verfassen der Publikation: 85%

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Erklärung

Ich versichere, dass ich die von mir vorgelegte Dissertation selbständig angefertigt, die benutzten Quellen und Hilfsmittel vollständig angegeben und die Stellen der Arbeit − einschließlich Tabellen, Karten und Abbildungen −, die anderen Werken im Wortlaut oder dem Sinn nach entnommen sind, in jedem Einzelfall als Entlehnung kenntlich gemacht habe; dass diese Dissertation noch keiner anderen Fakultät oder Universität zur Prüfung vorgelegen hat; dass sie − abgesehen von unten angegebenen Teilpublikationen − noch nicht veröffentlicht worden ist, sowie, dass ich eine solche Veröffentlichung vor Abschluss des Promotionsverfahrens nicht vornehmen werde. Die Bestimmungen der Promotionsordnung sind mir bekannt.
Die von mir vorgelegte Dissertation ist von Prof. Dr. Tim Mansfeldt betreut worden.

Nachfolgend genannte Teilpublikation liegen vor:

- Matern, K., Kletti, H., Mansfeldt, T. Chemical and mineralogical characterization of chromite ore processing residue from two recent Indian disposal sites. *Chemosphere (2016) 155:188-195.*
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