



# Solubility and transport of Cr(III) in a historically contaminated soil – Evidence of a rapidly reacting dimeric Cr(III) organic matter complex



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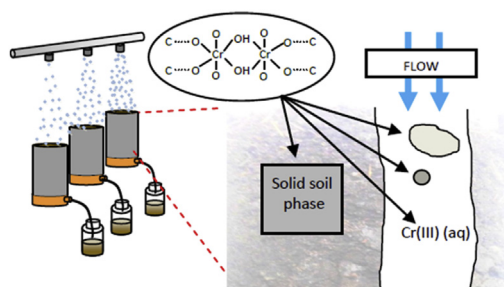
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## HIGHLIGHTS

- Dimeric Cr(III) bound to natural organic matter predominates in this soil.
- The dimeric Cr(III) species has fast dissolution kinetics.
- Solubility of dimeric Cr(III) was accurately described using a geochemical model.
- Mobilization of particle bound Cr(III) was independent of irrigation intensity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Chromium is a common soil contaminant and, although it has been studied widely, questions about its speciation and dissolutions kinetics remain unanswered. We combined information from an irrigation experiment performed with intact soil columns with data from batch experiments to evaluate solubility and mobilization mechanisms of Cr(III) in a historically contaminated soil (>65 years). Particulate and colloidal Cr(III) forms dominated transport in this soil, but their concentrations were independent of irrigation intensity ( $2\text{--}20\text{ mm h}^{-1}$ ). Extended X-ray absorption fine structure (EXAFS) measurements indicated that Cr(III) associated with colloids and particles, and with the solid phase, mainly existed as dimeric hydrolyzed Cr(III) bound to natural organic matter. Dissolution kinetics of this species were fast ( $\leq 1$  day) at low pH ( $< 3$ ) and slightly slower ( $\leq 5$  days) at neutral pH. Furthermore, it proved possible to describe the solubility of the dimeric Cr(III) organic matter complex with a geochemical equilibrium model using only generic binding parameters, opening the way for use of geochemical models in risk assessments of Cr(III)-contaminated sites.

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## 1. Introduction

Chromium (Cr) is a common soil contaminant that can originate from e.g., chromated copper arsenate salts (e.g., CCA) used for wood preservation (Jang et al., 2002; Hopp et al., 2008), chromite ores (Elzinga and Cirmo, 2010; Ding et al., 2016), industrial tanning

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(Landrot et al., 2012; Wang et al., 2016), Cr plating, and chemical waste landfill (Peterson et al., 1997). The two most common oxidation states for Cr in the environment are Cr(III) and Cr(VI). Cr(VI) is the thermodynamically favored species in “pure” aqueous solutions in the presence of oxygen (Ball and Nordstrom, 1998), although it has been shown that Cr(VI) easily can be reduced to Cr(III) by organic matter (OM) also under oxic conditions (Jardine et al., 1999; Tokunaga et al., 2001; Wittbrodt and Palmer, 1996).

Only a few studies have investigated the speciation of Cr in contaminated soils (Delsch et al., 2006; Ding et al., 2016; Elzinga and Cirno, 2010; Hopp et al., 2008; Landrot et al., 2012). In these studies, Cr has mainly been found as Cr(III) mineral precipitates, such as co-precipitates of Cr(III) and Fe(III) hydroxides (Delsch et al., 2006; Elzinga and Cirno, 2010; Hopp et al., 2008), Cr(III) hydroxides (Delsch et al., 2006; Ding et al., 2016), and chromite ( $\text{FeCr}_2\text{O}_4$ ) (Delsch et al., 2006; Elzinga and Cirno, 2010; Landrot et al., 2012; Peterson et al., 1997). However, due to the fairly high solubility of known Cr(III) minerals, such as  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}_2\text{O}_3$  ( $\log^*K_s = 9.35$  and  $8.52$ , respectively (Ball and Nordstrom, 1998)), and the strong binding of Cr(III) by OM (Gustafsson et al., 2014; Wittbrodt and Palmer, 1996) and hydrous ferric oxides (HFO) (Stumm, 1992), high levels of Cr(III) may be present in soils before any mineral precipitate is formed, i.e. in situations where the solubility of Cr(III) is controlled by sorption processes.

Some information exists on the binding mechanism of Cr(III) by isolated soil constituents, such as mixed clays (Sajidu et al., 2008), HFO (Charlet and Manceau, 1992), and natural organic matter (NOM) (Gustafsson et al., 2014). It is known that Cr(III) is adsorbed both to clays (Sajidu et al., 2008) and HFO (Charlet and Manceau, 1992) as oligomeric complexes. In a recent study, it was shown that Cr(III) formed a dimeric Cr-NOM complex at ambient pH (pH 5.6) and a monomeric Cr-NOM complex at low pH (pH  $\leq 2.3$ ) in an organic-rich soil spiked with  $\text{Cr}(\text{NO}_3)_3$ . Equilibrium was reached within a month at ambient pH, while longer equilibration times ( $\geq 90$  days) were required at low pH (Gustafsson et al., 2014). The slow reaction kinetics at low pH were explained by slow water exchange by the hydrated  $\text{Cr}^{3+}$  ion (Crimp et al., 1994; Gustafsson et al., 2014; Xu et al., 1985). Most soils contain a mixture of different sorbents that could all interact with Cr(III). At present, information regarding the speciation and coordination chemistry of Cr(III) in such systems is scarce, including the major sorbents involved in the binding of Cr(III) and the reaction kinetics of the corresponding sorption reactions.

In addition to the challenge in linking solid-phase speciation of Cr(III) to solubility and reaction kinetics, predicting Cr(III) leaching is further complicated by pronounced mobilization by colloids and particles (Gasser et al., 1994; Pedrot et al., 2008). A high concentration of NOM (Kaplan et al., 1993), high pH (Hu et al., 2008), and a coarse soil texture (Kjaergaard et al., 2004) have all been identified as soil factors promoting mobilization of particles and colloids. In contrast, the effect of rainfall intensity is less clear. The frequency and intensity of heavy precipitation events have probably already increased in parts of Europe and North America and are predicted to increase further in the near future (by 2100) as a result of climate change (Pachauri and Meyer, 2014). Some studies have indicated that the transport of particles and colloids increases with increasing irrigation intensity (Lægdsmand et al., 1999; Mohanty et al., 2015; Yin et al., 2010), while others have found no effect (Jacobsen et al., 1997). Thus, it is of major relevance to determine the effect of rainfall intensity on the mobilization of particles and colloids, because this in turn could have a significant effect on leaching of Cr from contaminated soils (Pedrot et al., 2008; Vogel et al., 2007).

The overall aim of this study was to investigate the mechanism(s) governing the solubility and mobility of Cr(III) in historically ( $>65$  yrs) contaminated soil. Specific objectives were to (i)

assess the speciation of Cr(III) in the colloidal, particulate, and solid soil phases, (ii) link the solubility and dissolution kinetics of Cr(III) to the solid-phase speciation and (iii) investigate the effect of irrigation intensity on mobilization of soluble, colloidal, and particulate Cr(III) under unsaturated conditions.

## 2. Material and methods

### 2.1. Soil samples

Four intact soil columns (20 cm in diameter, 30 cm deep measured from the soil surface) were collected from a site contaminated with copper (Cu), chromium, and arsenic (As) salts originating from wood impregnation activities during the period 1941–1952. The columns were sampled in 2013 using an excavator rigged with a drill head holding a PVC pipe. The pipe was pushed approximately 0.5 m into the soil and then lifted. In the laboratory, the columns were cut to 30 cm and the base of each column was carefully prepared, preserving the soil structure. The soil is a sandy loam and consists of an organic-rich top layer (0–4 cm) and a mineral layer (4–30 cm) lacking obvious differences in chemical or physical properties (Table S1).

### 2.2. Irrigation experiment

The columns were set up in an irrigation chamber (Liu et al., 2012) at 21 °C, allowing free drainage at the base. Polyamide cloth (mesh size 50  $\mu\text{m}$ ) was attached to the bottom of the columns to minimize soil losses. Subsequently three different irrigation intensities were simulated, corresponding to moderate (1.6–2  $\text{mm h}^{-1}$ , referred to hereafter as 2  $\text{mm h}^{-1}$ ), heavy (8–12  $\text{mm h}^{-1}$ , referred to as 10  $\text{mm h}^{-1}$ ), and extreme (19–22  $\text{mm h}^{-1}$ , referred to as 20  $\text{mm h}^{-1}$ ) intensity which created an unsaturated flow through the columns (Fig. S2). Artificial rainwater with a composition representative of natural rainwater in central Sweden (Table S2), and with ionic strength 0.055 mM and pH 5, was used for irrigation. Before the start of the irrigation experiment, the columns were pre-irrigated with 2  $\text{mm h}^{-1}$  until the electrical conductivity in the leachate, measured with a Cond3310 device (WTW GmbH Weilheim, Germany), remained stationary. The leachate was sampled four or five times in each irrigation intensity session, at 0.5–4.1 effective pore volumes ( $\text{PV}_{\text{eff}}$ ), where one  $\text{PV}_{\text{eff}}$  is the volume of the pores actively participating in transport, which in this case was equivalent to about 3.6 L. Elements and organic carbon (OC) in all leachate from the irrigation experiment were divided into three different operationally defined size fractions: particles (50–0.45  $\mu\text{m}$ ), colloids (0.45  $\mu\text{m}$ –10 kDa), and truly dissolved ( $<10$  kDa), using a membrane syringe filter (0.45  $\mu\text{m}$ , PALL Laboratory, Acrodisc® Supor®) or an ultra-centrifuge filter (10 kDa, PALL Laboratory, Macrosep® Advance) (see Fig. S1 for more details). The pH was measured in unfiltered samples using a PHM93 reference pH meter (Radiometer Copenhagen) equipped with a combination electrode. Total metal concentrations ( $<50$   $\mu\text{m}$ ) were measured after digestion by adding 1.2 mL suprapure nitric acid to 12 mL sample in an autoclave. All metal samples were preserved with 1% nitric acid and the concentrations were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) and/or inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). Concentrations of OC were measured on unfiltered, membrane-filtered, and ultra-filtered solutions, using infrared spectrophotometry. Anions were measured on filtered samples, using ion chromatography.

At the end of the irrigation experiment, all four columns were split into three layers. The organic-rich top layer (0–4 cm) was

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