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Laboratory investigations of the effects of nitrification-induced acidification on Cr cycling in vadose zone material partially derived from ultramafic rocks

Christopher T. Mills *, Martin B. Goldhaber

U.S. Geological Survey, Crustal Geophysics and Geochemistry Science Center, Building 20, MS964D, Denver Federal Center, Denver, CO 80225, United States

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ABSTRACT

Sacramento Valley (California, USA) soils and sediments have high concentrations of Cr(III) because they are partially derived from ultramafic material. Some Cr(III) is oxidized to more toxic and mobile Cr(VI) by soil Mn oxides. Valley soils typically have neutral to alkaline pH at which Cr(III) is highly immobile. Much of the valley is under cultivation and is both fertilized and irrigated. A series of laboratory incubation experiments were conducted to assess how cultivation might impact Cr cycling in shallow vadose zone material from the valley. The first experiments employed low (7.1 mmol N per kg soil) and high (35 mmol N kg^{-1}) concentrations of applied $(NH_4)_2SO_4$. Initially, Cr(VI) concentrations were up to 45 and 60% greater than controls in low and high incubations, respectively. After microbially-mediated oxidation of all NH_4^+, Cr(VI) concentrations dropped below control values. Increased nitrifying bacterial populations (estimated by measurement of phospholipid fatty acids) may have increased the Cr(VI) reduction capacity of the vadose zone material resulting in the observed decreases in Cr(VI). Another series of incubations employed vadose zone material from a different location to which low (45 meq kg^{-1}) and high (128 meq kg^{-1}) amounts of NH_4Cl, KCl, and $CaCl_2$ were applied. All treatments, except high concentration KCl, resulted in mean soil Cr(VI) concentrations that were greater than the control. High concentrations of water-leachable Ba^{2+} (mean 38 μmol kg^{-1}) in this treatment may have limited Cr(VI) solubility. A final set of incubations were amended with low (7.1 mmol N kg^{-1}) and high (35 mmol N kg^{-1}) concentrations of commercial liquid ammonium polyphosphate (APP) fertilizer which contained high concentrations of Cr(III). Soil Cr(VI) in the low APP incubations increased to a concentration of 1.8 μmol kg^{-1} (5× control) over 109 days suggesting that Cr(III) added with the APP fertilizer was more reactive than naturally-occurring soil Cr(III).

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1. Introduction

Chromium (VI) is a human carcinogen and irritant through inhalation exposure (Salnikow and Zhitkovich, 2007). There is also evidence that Cr(VI) is toxic through ingestion (Salnikow and Zhitkovich, 2007; Stout et al., 2008). Elevated concentrations of Cr(VI) in groundwater often result from industrial point sources, but significant concentrations of naturally-occurring Cr(VI) have been reported in groundwater (e.g. Ball and Izbicki, 2004; Fantoni et al., 2002; Gonzalez et al., 2005). The proposed cause of naturally elevated concentrations of dissolved Cr(VI) in many areas is weathering of Cr(III) from ultramafic rocks and its subsequent oxidation by manganese oxides (Bartlett and James, 1979; Fendorf and Zasoski, 1992; Oze et al., 2007).

California is a chromium rich province due to abundant exposures of ultramafic rocks (Krevor et al., 2009; Oze et al., 2007). Groundwater concentrations of Cr(VI) greater than 0.1 μM are reported from many regions of California and Cr(VI) concentrations sometimes approach or exceed the California MCL for total Cr in drinking water of 50 μg L^{-1} (0.96 μM) (Ball and Izbicki, 2004; Chung et al., 2001; Dawson et al., 2008; Gonzalez et al., 2005; Izbicki et al., 2008; Kulongoski et al., 2006; Land and Belitz, 2008; Mathany and Belitz, 2009). Given that California has recently established a non-regulatory public health goal of 0.02 μg L^{-1} (0.4 nM) for Cr(VI) in drinking water (California OEHHA, 2011) this issue is of concern for municipalities and water districts (Water Resources Association of Yolo County, 2007;).

The Sacramento Valley comprises the northern half of California's Central Valley and is bordered by mountain ranges with extensive ultramafic outcrops (Morrison et al., 2009; Oze et al., 2007). Weathering of these outcrops has resulted in soils and vadose zone sediments of the Southern Sacramento Valley that are consistently elevated in Cr (up to 42 mmol kg^{-1}) compared to the geometric mean (0.71 mmol kg^{-1}) for surface soils in the conterminous U.S. (Goldhaber et al., 2009; Mills et al., 2011; Morrison et al., 2009). Much of this Cr resides as Cr(III) in the source mineral chromite ($FeCr_2O_4$) but some Cr(III) is associated with iron oxides and clays (Mills et al., 2011; Morrison, 2010). This Cr(III) is slowly mobilized and oxidized by abundant reactive Mn oxides resulting in small

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* Corresponding author. Tel.: +1 303 236 5529.
E-mail address: cmills@usgs.gov (C.T. Mills).

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amounts of Cr(VI) in valley soils and sediments (Chung et al., 2001; Mills et al., 2011).

The Central Valley is intensively cultivated and most crops require irrigation due to the Mediterranean climate. This has led to increased groundwater recharge through the vadose zone and recharge water often contains high concentrations of nutrients derived from inorganic fertilizers (Bertoldi et al., 1991; Davisson and Criss, 1993; Jurgens et al., 2010). Previous studies have shown that irrigation and/or inorganic fertilizer application can affect the residence and mobility of naturally-occurring or contaminant trace metals in soil environments through cation exchange, anion exchange, complexation, or pH adjustment (Becquer et al., 2003; Jalali and Moharami, 2010; Jurgens et al., 2010; Liu et al., 2007; Raous et al., 2010; Tsadilas et al., 2005; Zaccheo et al., 2006). For one example, laboratory studies showed that both KCl and NH_4Cl treatments of a contaminated soil resulted in increased mobility of Cu, Ni, and Cr (Liu et al., 2007). For another example, a field study showed that movement of bicarbonate-rich irrigation water through the vadose zone mobilizes naturally-occurring U in shallow groundwater of the eastern San Joaquin Valley (the southern half of the Great Valley) (Jurgens et al., 2010).

Mills et al. (2011) showed increased rates of Cr(VI) generation from vadose zone material from the Sacramento Valley with the addition of HCl. The highest HCl treatment resulted in 6 times more Cr(VI) than in the control after two weeks incubation, but the pH in this treatment was only modestly lower (1.3 units) than the control. The authors proposed that acidification increased the mobility of Cr(III) and the likelihood of its oxidation on manganese oxides that were abundant in the material (Mills et al., 2011). Increased Cr(III) mobility may have resulted from dissolution of Cr(III) minerals due to lowered pH, or the exchange of H^+ or base cations for Cr(III) on the soil exchange complex.

The current study investigated the effects of the soil acidification process of nitrification on cycling of naturally-occurring Cr(III). Soils can be acidified as a result of several processes including atmospheric deposition of nitric and sulfuric acids and oxidation of pyrite-bearing material (Rice and Herman, 2012). However, in agricultural settings, microbial nitrification of NH_4^+ applied as a fertilizer is the most common source of acidity (Gandois et al., 2011; Rice and Herman, 2012). Acidity is produced in the first step of a two-step oxidation of NH_4^+ to NO_3^-.

$$NH_4^+ + 3/2O_2 \rightarrow NO_2^- + H_2O + 2H^+ \tag{1}$$

Mediated by autotrophic ammonia oxidizing bacteria (AOB). Autotrophic nitrite oxidizing bacteria (NOB) mediate the second step of the oxidation.

$$NO_2^- + 1/2O_2 \rightarrow NO_3^- \tag{2}$$

We incubated the same vadose zone material used by Mills et al. (2011) with two different concentrations of $(NH_4)_2SO_4$ for approximately four months. The incubations were monitored for indications of nitrification and Cr(VI) production including microbial membrane phospholipid fatty acids (PLFAs) attributed to AOB and NOB. We ran parallel incubations with the common NH_4^+ fertilizer, ammonium polyphosphate (10–34–0). This fertilizer contained considerable concentrations of trace metals, including Cr(III), likely derived from the phosphate source rock (Abed et al., 2008; Molina et al., 2009; Otero et al., 2005). This fertilizer was tested to assess the relative reactivity of fertilizer-derived Cr(III) with the naturally-occurring Cr(III) in the vadose zone material. Because soil acidification typically results in increased base cation activity in the soil solution, we also tested the effects of KCl and $CaCl_2$ additions on Cr(VI) generation.

2. Methods

2.1. Mixtures of vadose zone material

Cores Sl0 and S11 were collected in Yolo County in May, 2008 as part of a study to characterize the chemistry, including concentrations of Cr(VI), of soils and vadose zone material in the southern Sacramento Valley (Mills et al., 2011). Core S11(3.6 m depth) was collected from a field in the Yolo County Grasslands Regional Park (38.49773 N, 121.69153 W). Core S10 (4.0 m depth) was collected from a University of California Davis agricultural field that was not under cultivation (38.54137 N, 121.85432 W). The characteristics of samples from the two cores followed the type descriptions of the mapped soil series Brentwood silty clay loam (S11) and Yolo silt loam (S10). Core samples were not sieved or dried and were stored at 4° C. Samples from these cores were used to make two different mixtures of vadose zone material for incubation experiments. Mixture S11 was prepared in July 2008 and combined approximately equivalent weights of 9 samples collected between 1.0 and 3.6 m depth. The S10 mixture was prepared in Oct. 2008 and combined 8 samples collected between 1.0 and 4.0 m depth. The upper 1 m of each core was not used in making the mixtures to minimize reduction of Cr(VI) in the incubations by the higher concentrations of soil organic matter in this interval. Mixtures were homogenized by thorough mixing with a stainless steel spatula. Clumps larger than 2 mm diameter were broken up by mixing. Mixtures were stored at 4° C until use in incubations. Experiments using the S11 mixture were initiated in Aug. 2008 and those using S10 in April 2010.

Analysis of sulfate-leachable Cr(VI), Cr oxidation capacity, and total element chemistry for individual samples used to make the two mixtures were reported by Mills et al. (2011). In addition, two selective extractions were performed on the S10 samples to characterize trace metals associated with Mn oxides and Fe oxides (Mills et al., 2011). For this study, these two selective extractions (hydroxylamine hydrochloride to dissolve more reactive Mn oxides and citrate–bicarbonate–dithionite to dissolve more reactive Mn and Fe oxides) were performed on subsamples from the S11 mixture to determine concentrations of trace elements associated with these two operationally-defined fractions. Details of these extraction procedures are described by Mills et al. (2011) as modified from Neaman et al. (2008). Also for this study, PLFA analyses were performed on select samples from the S11 core that were stored at −20° C.

2.2. Long-term (109 to 132 days) experiments with $(NH_4)_2SO_4$ and APP

Fifty mesocosms of the S11 mixture were prepared; the number was limited by the amount of material available. These consisted of eight replicated mesocosms of the unsterilized S11 material and two of sterilized material for each of five different treatments: control (C), low and high concentration ammonium sulfate (LS and HS), and low and high concentration APP (LP and HP). Stock solutions of $(NH_4)_2SO_4$ (ACS certified, Fisher Scientific) and liquid APP (Simplot 10–34–0) were made with ultrapure water. Solutions 0.5 M and 2.5 M in NH_4^+ were made for low and high concentration treatments of both $(NH_4)_2SO_4$ and APP. These solutions were filter-sterilized (0.2 μm pore size). The concentrations of APP solutions were based on 1.16 lb of nitrogen per gallon in the fertilizer concentrate as specified by the product data sheet.

Unsterilized mesocosms were established by placing 70 g of the vadose zone mixture S11 into a sterilized glass 250 mL Erlenmeyer flask and covering it with Parafilm M to minimize moisture loss. The moisture content of the mixture was 14.6 wt.%. Sterilized mesocosms were prepared identically but with vadose zone material that had been autoclaved (115° C) for three 30 minute intervals. Autoclaving resulted in drier material which was brought back to the original moisture content with sterilized ultrapure water. 850 μL of the appropriate stock solution or ultrapure water (C treatment) was added to each mesocosm