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Isotope evidence of hexavalent chromium stability in ground water samples

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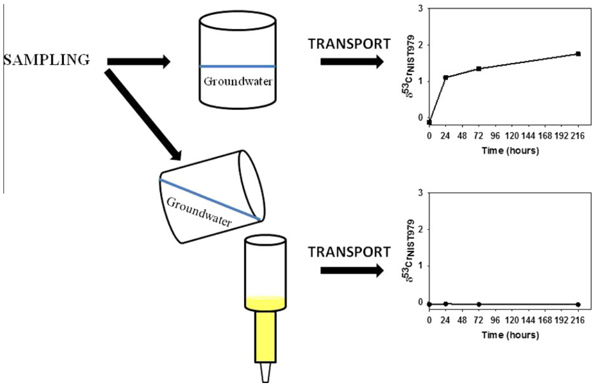
HIGHLIGHTS

- Cr(VI) reduction modified strongly Cr isotope ratios within 24 h after sampling.
- On-site preservation recommended by commonly available methods is not sufficient.
- Water samples should be processed on-site through anion column chemistry.

GRAPHICAL ABSTRACT



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ABSTRACT

Chromium stable isotopes are of interest in many geochemical studies as a tool to identify Cr(VI) reduction and/or dilution in groundwater aquifers. For such studies the short term stability of Cr(VI) in water samples is required before the laboratory analyses can be carried out. Here the short term stability of Cr(VI) in groundwater samples was studied using an isotope approach.

Based on commonly available methods for Cr(VI) stabilization, water samples were filtered and the pH value was adjusted to be equal to or greater than 8 before Cr isotope analysis. Based on our Cr isotope data (expressed as $\delta^{53}Cr_{NIST979}$), Cr(VI) was found to be unstable over short time periods in anthropogenically contaminated groundwater samples regardless of water treatment (e.g., pH adjustment, different storage temperatures). Based on our laboratory experiments, $\delta^{53}Cr_{NIST979}$ of the Cr(VI) pool was found to be unstable in the presence of dissolved Fe(II), Mn(IV) and/or SO_2. Threshold concentrations of Fe(II) causing Cr(VI) reduction range between 10 mg L^{-1} and 100 mg $L^{-1}$and less than 1 mg L^{-1} for Mn. Hence our isotope data show that water samples containing Cr(VI) should be processed on-site through anion column chemistry to avoid any isotope shifts.

1. Introduction

Chromium occurs naturally in water in either the Cr(III) or Cr(VI) oxidation state, where concentration of Cr(III) is limited by its solubility at the pH of most natural waters. Whereas Cr(III) is an essential micronutrient in human and animal diet, Cr(VI) is considered to be potentially carcinogenic and is associated with industrial activities such as production of stainless steel, plating of metals, pigments, leather processing, catalysts, surface treatments, and refractories (APHA-AWWA-WEF, 1999; Papp and Lipin, 2001). More than 200 companies in the Czech Republic use chromium and

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its compounds (tens of tons of chromium per year). Even though new environmentally-friendly technologies have been implemented, Cr(VI) is released to the environment and consequently may cause environmental risk to groundwater and ultimately human health (Holmes et al., 2008; Salnikow and Zhitkovich, 2008).

In contrast with Cr(III), Cr(VI) is highly soluble and mobile in water in the forms $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ (Palmer and Wittbrodt, 1991). Cr(VI) reduction via natural attenuation occurs commonly and depends mainly on reduction potential Eh, pH conditions (Palmer and Puls, 1994), presence of Fe(II) bearing minerals (Ellis et al., 2002), organic carbon (Trebien et al., 2011) and microorganisms (Mishra et al., 2010; Sikora et al., 2008). Mass-dependent fractionation of Cr isotopes occurs during Cr(VI) reduction and results in an enrichment in ^{53}Cr relative to ^{52}Cr in the remaining dissolved Cr(VI) fraction (Ellis et al., 2004), which gives us an effective tool to study Cr(VI) reduction in contaminated water.

Cr(VI) is relatively easily reduced to Cr(III) under certain conditions (Basu and Johnson, 2012; Saputro et al., 2014; Trebien et al., 2011), hence collection and sample preparation play an important role in Cr(VI) determination. The APHA–AWWA–WEF (American Public Health Association, American Water Works Association, Water Environment Federation; 1999) and US EPA methods for determination of Cr(VI) advise field preservation of the sample using NaOH (to adjust pH > 8) in order to provide sample stability. Nevertheless, Kumar and Riyazuddin (2009) found that such on-site preservation is not sufficient and determination of chromium may cause analytical problems due to sorption and fixation of chromium species onto Fe(III) hydroxides and other precipitates.

The aim of this study is to investigate Cr isotope stability over time in groundwater samples that have been either untreated or treated on-site according to US EPA (1996) and/or APHA-AWWA-WEF (1999) methods and also in laboratory samples.

2. Materials and methods

2.1. Reagents and materials

All chemicals ($K_2Cr_2O_7$, $(NH_4)_2Fe(SO_4)_2.6H_2O$, MnO_2) used in laboratory experiments were analytically pure. Ultrapure chemicals Romil or Rotipuran (HCl, HNO_3, NH_4OH, H_2O_2) were used for sample preparation and purification. All beakers, storage bottles, filtration apparatus etc. were acid-cleaned in 10% (v/v) HNO_3 (double-distilled) overnight.

2.2. Sample collection

Groundwater samples were collected in the industrial area of a company producing components for bicycles operating with chrome plating in Loučná nad Desnou (in the north-east of the Czech Republic). Groundwaters were collected from permanent monitoring wells (physico-chemical characteristics are shown in Table 1) and treated on-site. The anion exchange columns were prepared for the sampling on-site in the laboratory (see Section 2.4). At first sampling campaign, samples were taken to determine Cr concentrations in groundwater. Thereafter, samples were sampled again, filtered (0.45 μm) and subsequently a water aliquot containing approx. 2 μg Cr(VI) was processed through the anion exchange column to obtain a sample representing the true Cr isotope composition (without an effect of possible Cr(VI) reduction on Cr isotopes). In addition, 4L of groundwater was sampled and filtered immediately. A 2L aliquot was adjusted to pH 9 (NH_4OH addition) and divided in two 1L-PE bottles. The first bottle was kept under 5 °C, while the second was stored under laboratory conditions (22 °C). The remaining 2L of the filtered sample were divided the same way (laboratory temperature vs. refrigerated samples) but without any pH adjustment. Water aliquots containing 2 μg Cr(VI) were processed through column chromatography following a given time schedule (24 h, 72 h, 120 h and 168 h) to test the stability of Cr isotopes in groundwater samples.

2.3. Laboratory experiment

In laboratory experiments $K_2Cr_2O_7$ (Sigma–Aldrich, analytical grade) was used to test three hypotheses. Based on results found by Kitchen et al. (2012) our first hypothesis was that Fe(II) addition in different concentrations causes Cr(VI) reduction associated with a Cr isotope shift over time. The second hypothesis, based on a US EPA (2000) report and on studies performed by Bain and Bullen (2005) and Trebien et al. (2011), was that different concentrations of added MnO_2 can oxidize Cr(III) and consequently cause a Cr isotope shift. The last hypothesis, based on a precipitation experiment performed by Schoenberg et al. (2008), was that precipitation of $Cr_2(SO_4)_3$ (enriched in heavy Cr isotopes) resulting from addition of SO_2 to dissolved $K_2Cr_2O_7$ causes a shift in $\delta^{53}Cr_{NIST979}$ to lighter values for Cr in the remaining liquid sample.

All experiments were carried out at room temperature (approx. 22 °C). $K_2Cr_2O_7$ was dissolved in ultrapure H_2O (Milli-Q System, $<1 \times 10^{-18}\ \Omega\ cm^{-1}$, UV lamp for organic residues destruction) to reach a final Cr concentration of 100 mg L^{-1}, and aliquots containing 2 μg Cr were processed through an anion exchange column (see Section 2.4) immediately and after 24 h, 72 h, and 216 h to represent samples without additional treatment. The same amount of $K_2Cr_2O_7$ was dissolved and processed through an anion column immediately and after 24 h, 72 h, and 216 h after addition of: (i) $(NH_4)_2Fe(SO_4)_2.6H_2O$ with the final Fe concentration of 10 mg L^{-1} (this compound was chosen due to the high stability of Fe^{2+}), (ii) $(NH_4)_2Fe(SO_4)_2.6H_2O$ with the final Fe concentration of 100 mg L^{-1}, (iii) SO_2 (200 mL of $K_2Cr_2O_7$ was purged with SO_2 at 340 mL min^{-1} for 15 min. The conditions were previously examined empirically and the reaction time was prolonged to ensure complete Cr(VI) reduction), (iv) SO_2 with MnO_2 addition with the final Mn concentration of 50 mg L^{-1} (v) MnO_2 with the final Mn concentration of 1 mg L^{-1} and (vi) MnO_2 with the final Mn concentration of 50 mg L^{-1}. All solutions were adjusted to a pH value of 7 to mimic natural on-site conditions.

An additional experiment concerning MnO_2 addition to oxidize Cr(III) was performed in a different manner. $K_2Cr_2O_7$ was dissolved in ultrapure 6 M HCl and Cr(VI) was subsequently reduced to Cr(III) by addition of ultrapure H_2O_2 (Bullen, 2007). Solution was left overnight to ensure sufficient Cr(VI) reduction and further left on a hot plate to assure complete removal of H_2O_2. The sample was converted to 1L solution by addition of ultrapure H_2O and the pH value was adjusted to 7. An aliquot containing 2 μg Cr (representing the initial value at the sampling time 0) was taken and evaporated near to dryness, HNO_3 was added drop wise to remove chlorides and the sample was then prepared for multicollector-inductively coupled plasma mass spectrometry analysis (MC ICP MS). MnO_2 was then added to the solution resulting in Mn concentrations of 1 mg L^{-1} and 50 mg L^{-1} and the solutions were processed through anion exchange columns after 24 h, 72 h and 216 h.

The additional experiment concerning SO_2 and MnO_2 addition was performed based on the results of previous experiments. It was done as follows: the previously prepared solution with SO_2 addition was used as an initial solution and MnO_2 was added to give a final Mn concentration of 50 mg L^{-1} (the initial value represented $\delta^{53}Cr_{NIST979}$ value of sample sampled 624 h after SO_2 addition). Cr(VI) presented in the initial solution exhibited Cr