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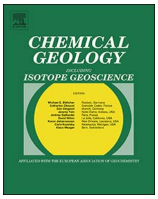

Comparison of $\delta^{53}Cr_{Cr(VI)}$ values of contaminated groundwater at two industrial sites in the eastern U.S. with contrasting availability of reducing agents

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ABSTRACT

Natural attenuation of groundwater contaminated by toxic hexavalent chromium [Cr(VI)] was studied at two industrial sites in the eastern U.S. Concentration and isotope composition of the residual Cr(VI) were determined at site A in Connecticut whose aquifer was polluted by electroplating solutions between 1930 and 1995, and at site B in New Jersey whose aquifer was polluted by soluble chromium-processing wastes between 1911 and 1963. Site A was characterized by lower mean Cr(VI) concentrations ($2\,mg\,L^{-1}$) and lower mean $\delta^{53}Cr_{Cr(VI)}$ values (1.84‰) in groundwater than site B ($200\,mg\,L^{-1}$ and 2.89‰, respectively). $\delta^{53}Cr_{Cr(VI)}$ values were strongly positively correlated with dissolved organic carbon (DOC; $p = 0.002$), but not with dissolved ferrous iron [Fe(II)], or divalent manganese [Mn(II)], indicating that DOC may have played a major role in spontaneous reduction of the mobile carcinogenic Cr(VI) to immobile non-toxic Cr(III). At site B, the supply of DOC may be nearly unlimited, due to the presence of a buried organic meadow mat at a depth of six meters below the ground surface. At site A, contaminated groundwater has been extracted and treated since 1995. The mean $\delta^{53}Cr_{Cr(VI)}$ values of the residual aqueous contamination at site A significantly decreased over the past 15 years ($p < 0.05$), possibly suggesting re-oxidation and remobilization of previously precipitated pollutant Cr.

1. Introduction

Hexavalent chromium [Cr(VI)] has generated much interest due to its extreme toxicity and mobility (Palmer and Puls, 1994; Ellis et al., 2002; Ball and Izbicki, 2004; Berna et al., 2010; Basu and Johnson, 2012; Wanner et al., 2012; Izbicki et al., 2015; Manning et al., 2015). Geological reservoirs mostly contain the non-toxic, immobile trivalent form of Cr (Stanin, 2005; Economou-Eliopoulos et al., 2014). Oxidation of trivalent chromium [Cr(III)] to the carcinogenic Cr(VI) form proceeds not only during weathering (D'Arcy et al., 2016), but, much more importantly, is part of various technological processes (Losi et al., 1994; Izbicki et al., 2008, 2012; Jamieson-Hanes et al., 2012). The predominant Cr(VI) species are chromate (CrO_4^{2-}), hydrochromate ($HCrO_4^{-}$), and dichromate ($Cr_2O_7^{2-}$; Losi et al., 1994).

Chromium has four stable isotopes (^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr), and their abundance ratios can be used as a diagnostic tool in biogeochemical and toxicological studies (Schoenberg et al., 2008; Berna et al., 2010). Usually, the ratio of the two most abundant Cr isotopes, $^{53}Cr/^{52}Cr$, is measured by mass spectrometry and expressed in $\delta^{53}Cr$ notation as a ‰ deviation of the Cr isotope composition of the sample from the Cr isotope composition of a standard. Chromium isotope fractionations are driven by redox reactions more than by adsorption, diffusion, or any other physical process (Ellis et al., 2002, 2004). Two types of Cr isotope applications have emerged as the most successful: (i) Cr isotope systematics can provide insights into oxygen concentrations in the Precambrian atmosphere (Frei et al., 2009; Crowe et al., 2011,

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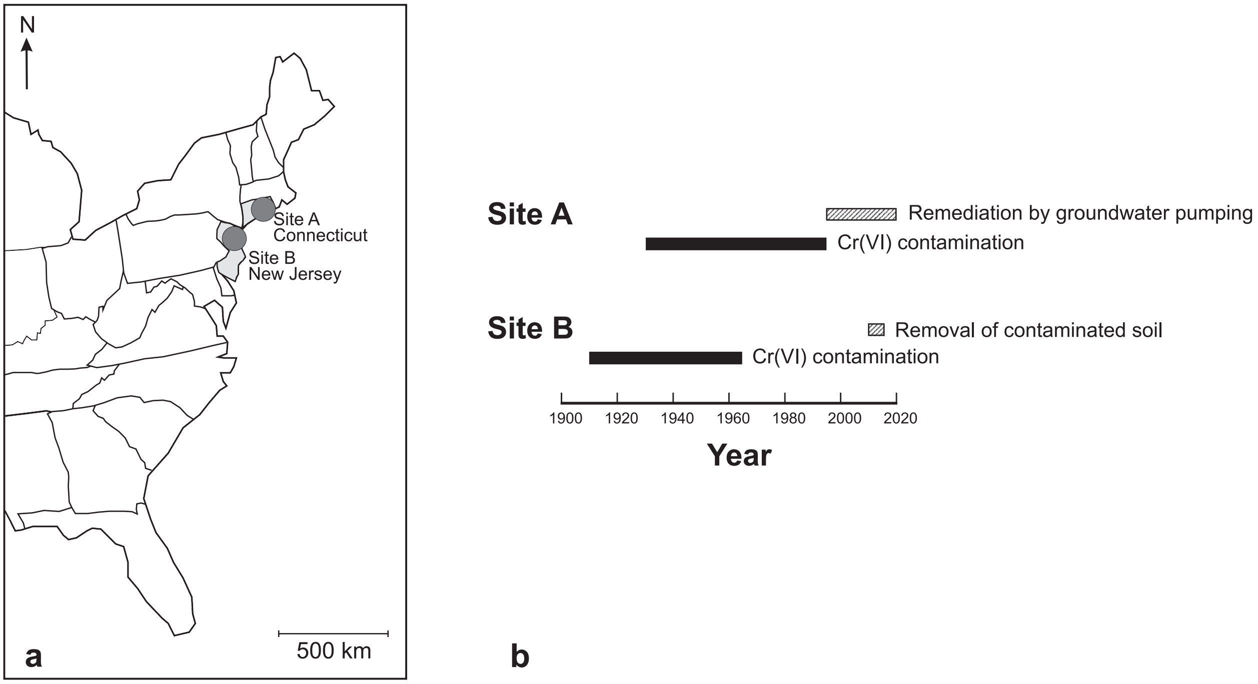

Fig. 1. Location and pollution history of the study sites. (a) Schematic map, (b) time line for each study site.

2013; Planavsky et al., 2014; Gilleaudeau et al., 2016), and (ii) Cr isotope fractionations can indicate the extent of natural attenuation of Cr(VI)-contaminated groundwaters (Ellis et al., 2002; Izbicki et al., 2008, 2012; Raddatz et al., 2011; Berna et al., 2010; Novak et al., 2014, 2017c).

Theoretical Cr isotope fractionations associated with equilibrium processes tend to be larger than those accompanying kinetic processes (Schauble et al., 2004). At the same time, isotope fractionations associated with Cr(VI) reduction tend to be larger than those accompanying Cr(III) oxidation on mineral surfaces (Ellis et al., 2002; Sikora et al., 2008; Zink et al., 2010; Døssing et al., 2011; Kitchen et al., 2012; Frei and Polat, 2012; Frei et al., 2014; Wang et al., 2015; D'Arcy et al., 2016). In natural settings, oxidation of geogenic Cr(III) is a very slow equilibrium process, whereas reduction of dissolved Cr(VI) is a relatively fast kinetic process. Both result in isotopically heavier Cr(VI) in the aqueous form (Wang et al., 2015). In the case of oxidation of solid Cr(III), the solution is a reaction product. In contrast, in case of reduction of aquatic Cr(VI), the solution is a residual reactant (Zink et al., 2010). One prerequisite for the equilibrium Cr isotope fractionation during Cr(III) oxidation is that the mineral surfaces are in long-term contact with Cr(VI)-containing solutions (Wang et al., 2015). The kinetic effect during oxidation of solid Cr(III) is negligible because each layer of the lattice is completely oxidized and removed (Qin and Wang, 2017).

Industrial Cr(VI) contamination of vegetation, soil, bedrock, surface water and groundwater results from leakage of industrial solutions from plating shops and tanneries (Blowes et al., 1997). Hexavalent chromium from Cr ore-processing wastes can also contaminate soil and groundwater. Several authors have shown that contaminated groundwaters may contain isotopically relatively heavy Cr(VI) (Ellis et al., 2002; Izbicki et al., 2008, 2012; Berna et al., 2010; Wanner et al., 2012; Novak et al., 2014, 2017b). The high δ^{53}Cr values have been interpreted as a result of natural attenuation of Cr(VI)-contaminated groundwater. Aqueous chromium is removed by Cr(III) precipitation following spontaneous Cr(VI) reduction. Because of a kinetic isotope fractionation, the reaction product Cr(III) becomes isotopically lighter, while the residual aqueous Cr(VI) becomes isotopically heavier (Ellis et al., 2002; Sikora et al., 2008; Zink et al., 2010; Kitchen et al., 2012; Basu and Johnson, 2012). Chromium isotope fractionations inferred from observations of natural groundwater systems tend to be lower than those determined by laboratory experiments, complicating quantification of the amount of Cr(VI) removed from the aquifer (see Izbicki et al., 2008, 2012 for detailed discussion). Information on natural attenuation of contaminated groundwater is important for facility owners and authorities responsible for environmental protection. If sufficiently fast and efficient, natural attenuation could represent an alternative to the costly conventional pump-and-treat approach in Cr polluted industrial areas (Richard and Bourg, 1991).

Laboratory and field-based studies have indicated that Cr(VI) reduction in aquifers can be biologically mediated (Kitchen et al., 2012; Dimitroula et al., 2015). Abiotic reducers may also play an important role (Qin and Wang, 2017). Common Cr(VI) reducers include bacteria, particulate or dissolved organic substances (humic acids), sulfides [S (II)], dissolved ferrous iron [Fe(II)], dissolved divalent manganese [Mn (II)], and Fe(II)-bearing minerals (Eary and Rai, 1988; Fendorf and Zasoski, 1992; Wielinga et al., 2001; Ndung'u et al., 2010; Døssing et al., 2011; Birkner and Navrotsky, 2012). As Cr(VI) reduction proceeds, higher $\delta^{53}Cr_{Cr(VI)}$ values should accompany decreasing Cr(VI) concentrations in the groundwater. However, most industrial sites lack this simple negative correlation (Izbicki et al., 2012). It is now well established that the concentration and isotope composition of Cr(VI) in industrially contaminated aquifers is also affected by advection of heterogeneous plumes, mixing with more/less contaminated groundwater, and Cr(VI) adsorption on mineral surfaces (Ellis et al., 2002). No study thus far has focused on the correlation between availability of reducing agents and $\delta^{53}Cr_{Cr(VI)}$ values in Cr(VI)-contaminated groundwater.

The current study reports Cr(VI) concentration and isotope systematics in contaminated groundwater from two industrial sites in the eastern U.S. in light of the relative availability of dissolved organic carbon (DOC), Fe(II) and Mn(II) at each site. It is reasonable to assume that the δ^{53}Cr values of the industrial solutions released into the environment at both sites were close to 0‰ (Schoenberg et al., 2008; Novak et al., 2017a). This enabled a statistical evaluation of the relationships between the abundance of individual reducing agents and the shift to higher δ^{53}Cr values of the residual groundwater. The effect