



# Isotopic evidence for reduction of anthropogenic hexavalent chromium in Los Alamos National Laboratory groundwater



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## ABSTRACT

Reduction of toxic Cr(VI) to less toxic Cr(III) is an important process for attenuating Cr(VI) transport in groundwater. This process results in immobilization of chromium as Cr(III) and effectively decreases the overall mobility of the chromium inventory. During both abiotic and biotic reduction of Cr(VI) to Cr(III), a kinetic isotope effect occurs in which the lighter isotope, <sup>52</sup>Cr, reacts preferentially, leaving the remaining dissolved Cr(VI) enriched in the heavier isotope, <sup>53</sup>Cr. Cr isotopes have proven to be a useful tool for estimating the magnitude of Cr(VI) reduction and for determining where in a hydrologic system reduction is occurring. In this paper, we discuss patterns of reduction in perched-intermediate and regional aquifer systems contaminated with Cr(VI) related to historical use of potassium dichromate as an anticorrosion agent in cooling towers at a power plant at the Los Alamos National Laboratory in northern New Mexico. We utilize Cr isotopes to assess the relative effects of mixing and reduction on measured  $\delta^{53}\text{Cr}$  in groundwater, with an emphasis on where in the system reduction occurs. Chromium isotope measurements provide strong evidence for reduction of Cr(VI) in vadose zone basalts.

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## 1. Introduction

Reduction of toxic Cr(VI) to less toxic Cr(III) is an important process for attenuating Cr(VI) transport in groundwater (Eary and Rai, 1989; Palmer and Wittbrodt, 1991; Palmer and Puls, 1994; Davis and Olsen, 1995). This process results in immobilization of chromium as Cr(III) and effectively decreases the overall mobility of the chromium inventory. Cr isotopes have proven to be a useful tool for estimating the magnitude of Cr(VI) reduction and for determining where in a hydrologic system reduction is occurring (Blowes, 2002; Ellis et al., 2002; Izbicki et al., 2008, 2012; Berna et al., 2010; Gao et al., 2010; Raddatz et al., 2011; Wanner et al., 2012a, 2012b).

The use of Cr isotopes to estimate the magnitude of Cr(VI) reduction along a flow path relies on the fact that during both abiotic and biotic reduction of Cr(VI) to Cr(III), a kinetic isotope effect occurs in which the lighter isotope, <sup>52</sup>Cr, reacts preferentially, leaving the remaining dissolved Cr(VI) enriched in the heavier isotope, <sup>53</sup>Cr (e.g. Ellis et al., 2002; Johnson and Bullen, 2004; Izbicki et al., 2008; Berna et al., 2010; Jamieson-Hanes et al., 2012b). The most common model used to determine the extent of reduction based on the  $\delta^{53}\text{Cr}$  of Cr(VI) is the Rayleigh model (Ellis et al., 2002; Berna et al., 2010; Zink et al., 2010; Dossing et al., 2011; Raddatz et al., 2011) that can be closely approximated as

$$\delta = \delta_0 - \epsilon \ln(f) \quad (1)$$

(see Supplementary Information for an explanation of delta notation) where  $\delta$  is the measured  $\delta^{53}\text{Cr}$  value,  $\delta_0$  is the initial  $\delta^{53}\text{Cr}$  value prior to any reduction,  $f$  is the fraction of the original Cr(VI) remaining, and  $\epsilon$  expresses the magnitude of isotopic fractionation (Raddatz et al., 2011).  $\epsilon$  can be expressed in per mil form and approximated as

$$\epsilon = \delta^{53}\text{Cr}_{\text{reactant}} - \delta^{53}\text{Cr}_{\text{product}} \quad (2)$$

Application of the Rayleigh model to determine the magnitude of Cr(VI) reduction can be considered semi-quantitative as a range of

*Abbreviations:* LANL, Los Alamos National Laboratory; RLWTF, Radioactive Liquid Waste Treatment Facility; TA, Technical Area.

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experimental  $\epsilon$  values has been determined in laboratory experiments using inorganic and organic reductants and biotic and abiotic reduction mechanisms. The range of Cr isotopic fractionation determined in batch and column experiments is  $\epsilon = 0.4$  to 5‰ (Ellis et al., 2002; Sikora et al., 2008; Berna et al., 2010; Zink et al., 2010; Dossing et al., 2011; Basu and Johnson, 2012; Han et al., 2012; Jamieson-Hanes et al., 2012b; Kitchen et al., 2012). Fractionation tends to be smaller in cases of rapid Cr(VI) reduction (Kitchen et al., 2012), anaerobic microbial reduction (Sikora et al., 2008), reduction during porous flow (in column studies) (Jamieson-Hanes et al., 2012a, 2012b), and when there is addition of fresh reductant at constant mass flux (Dossing et al., 2011). Additionally,  $\epsilon$  values determined based on field experiments tend to fall on the lower end of the observed range of laboratory-derived values (Berna et al., 2010; Izbicki et al., 2012; Wanner et al., 2012a). If actual aquifer fractionation is lower than assumed by applying Eq. (1), the degree of reduction will be underestimated. Since the particular reduction mechanism and associated  $\epsilon$  value are typically unknown for a given groundwater setting, there is considerable uncertainty in estimation of the magnitude of reduction (Jamieson-Hanes et al., 2012a, 2012b). Cr isotope measurements, however, still provide important bounds on the degree of natural reduction in groundwater systems, including where in the system reduction is most prevalent.

Chromium isotopic fractionation does not appear to vary with Cr(VI) concentration, at least in the case of microbial reduction (Sikora et al., 2008). In addition, there does not appear to be isotopic exchange between Cr(III) and Cr(VI) on short timescales of days to weeks (Zink et al., 2010). Also, Cr isotopes are not fractionated significantly by sorption processes (Ellis et al., 2004).

In some settings, mixing of natural and anthropogenic Cr(VI) must be considered (e.g. Raddatz et al., 2011). Recent work suggests that water–rock interactions during weathering of mafic rocks result in the production of natural Cr(VI) with elevated  $\delta^{53}\text{Cr}$  (Izbicki et al., 2008). Alternatively, elevation of  $\delta^{53}\text{Cr}$  in naturally-sourced dissolved Cr(VI) can occur after Cr(VI) “is delivered to the water, via partial reduction by Fe(II)-bearing solids or bacteria” (Raddatz et al., 2011). Chromite ores, from which industrial Cr is derived, have an average  $\delta^{53}\text{Cr}$  of  $-0.082 \pm 0.058\%$  ( $2\sigma$ ) (Schoenberg et al., 2008). Because of the high temperature and efficiency of Cr extraction from ore, industrial Cr should have very similar  $\delta^{53}\text{Cr}$  values to chromite ore (Ellis et al., 2002; Schoenberg et al., 2008). The highest value measured in industrial reagent Cr was 0.37‰ (Ellis et al., 2002). Uncertainty in the  $\delta^{53}\text{Cr}$  of the industrial source adds further uncertainty in calculating the degree of Cr(VI) reduction occurring along a flow path.

At present, only a small number of case studies have been published to describe application of Cr isotopes in practical field studies. Herein, we discuss patterns of reduction in perched-intermediate and regional aquifer systems contaminated with Cr(VI) related to historical use of potassium dichromate as an anticorrosion agent in cooling towers at a power plant at the Los Alamos National Laboratory (LANL) in northern New Mexico. Potassium dichromate was a common industrial corrosion inhibitor when it was used at LANL. The subsurface stratigraphy in this setting includes basalts with Fe(II)-bearing minerals and other rock types where natural attenuation via reduction of Cr(VI) may occur. Cr(VI) reduction in basalts at the Idaho National Laboratory has been suggested based on evidence from Cr isotopes (Raddatz et al., 2011). Natural Cr(VI) occurs in groundwater at the LANL site (Dale et al., 2013), so the effect of mixing between natural and anthropogenic sources must be considered. We apply the approach utilized by Raddatz et al. (2011) to assess the relative effects of mixing and reduction on measured  $\delta^{53}\text{Cr}$  in LANL groundwater, with an emphasis on where in the system reduction occurs.

### 1.1. Discharge of hexavalent chromium and other contaminants

Fig. 1 shows the location of liquid outfalls relevant to this investigation. Liquid effluents have been discharged to Sandia Canyon since the

early 1950s at Outfall 001. The highest volume releases include treated sanitary wastewater, steam plant effluent, and cooling tower blowdown from the LANL Technical Area 3 (TA-03) power plant. Potassium dichromate was used from 1956 to 1972, and resulted in an estimated total release of 31,000 to 72,000 kg of Cr(VI) into upper Sandia Canyon. Outfall discharge during this period is estimated at 0.4 to 1.1 million liters per day. Recent outfall discharge to upper Sandia Canyon is approximately 0.8 to 1.5 million liters per day, providing sufficient water to mobilize contaminants within the watershed (LANL, 2009, 2012).

Contaminant discharges to Mortandad Canyon, located to the south of Sandia Canyon (Fig. 1), are also relevant to this investigation due to the potential for mixing with waters originating in Sandia Canyon. Water treatment at LANL's Radioactive Liquid Waste Treatment Facility (RLWTF) began in July 1963. The RLWTF discharged treated wastewater containing perchlorate, nitrate and tritium, but not Cr(VI), to Mortandad Canyon through Outfall 051 via a tributary called Effluent Canyon. However, a smaller chromium source (based on the occurrence of Cr(III) in sediments) of unknown provenance also occurs in Effluent Canyon upgradient from Outfall 051. Outfall 051 has historically released much lower volumes of effluent than Outfall 001 with peak discharges of 0.2 million liters per day occurring in 1968. Discharges from Outfall 051 decreased significantly after the mid-1980s and effectively ended in late 2010 (LANL, 2009, 2012).

### 1.2. Conceptual model for chromium transport

This section is summarized from recent regulatory reports submitted to the New Mexico Environment Department (LANL, 2009, 2012; reports are publicly available (see <http://www.lanl.gov/community-environment/environmental-stewardship/public-reading-room.php>); see also Birdsell et al. (2005) and Vesselinov et al. (2013)). LANL groundwater data may be accessed online at [www.intellusnm.com](http://www.intellusnm.com).

A significant portion of the Cr(VI) released from Outfall 001 to Sandia Canyon was immobilized as Cr(III) in a wetland present in the upper part of Sandia Canyon (Fig. 1). The estimated total inventory of contaminant chromium in sediment deposits in Sandia Canyon is 18,000 kg, with measured concentrations ranging from 5.6 mg/kg to 3740 mg/kg (LANL, 2007). Approximately eighty-five percent of this total is concentrated in sediments within the Sandia Canyon wetland. Chromium in wetland sediments is nearly 100% Cr(III) based on paired analyses of total Cr and Cr(VI) (LANL, 2007).

A water balance study in Sandia Canyon showed that most surface water passes through the wetland area, with less than 2% of the water lost to evapotranspiration and infiltration (LANL, 2009). After exiting the wetland, surface water flows without loss approximately 0.85 km down a narrow slot canyon underlain by relatively impermeable welded tuff with little or no alluvial sediments. About 20% of the surface water infiltrates the canyon floor between 0.85 and 3.6 km east of the wetland. Approximately 60% infiltrates 3.6 to 4.5 km east of the wetland where the canyon gradually widens and alluvial deposits become about 20 m thick. The infiltrated surface water forms a perched alluvial groundwater system that extends down canyon approximately 2.2 km (Fig. 1, Supplementary Fig. 1). The alluvial groundwater drains into the suballuvial bedrock tuffs that are poorly welded and more porous in this part of the canyon. Flow into the suballuvial bedrock is spatially and temporally heterogeneous with percolation rates potentially as high as a few meters per year, resulting in travel times to the regional aquifer from 5 to 50 years with best estimates ranging between 20 to 30 years. Deeper percolation of alluvial groundwater as unsaturated flow provides a driving force for subsurface transport of mobile constituents, including Cr(VI).

From the alluvial zone, water percolates down through the vadose zone, consisting of Bandelier Tuff Formation volcanic rocks and Puye Formation sediments, where perching horizons on top of and within Cerros del Rio basalts cause some water to move laterally (Supplementary Fig. 1; For a detailed description of site geology see Broxton and Vaniman,

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