Chromium isotope fractionations resulting from electroplating, chromating and anodizing: Implications for groundwater pollution studies

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ABSTRACT

A number of shallow aquifers in industrial regions have been polluted by toxic Cr(VI). At some sites, spontaneous reduction of dissolved Cr(VI) to insoluble Cr(III) has been observed. Precipitation of non-toxic Cr(III) is accompanied by a Cr isotope fractionation, with the residual Cr(VI) becoming enriched in the heavier isotope ^{53}Cr , and depleted in the lighter isotope ^{52}Cr . Thus far, $\delta^{53}\text{Cr}$ values of the contamination source have been poorly constrained. These values are needed to quantify the extent of Cr(VI) reduction in the aquifers. We present $\delta^{53}\text{Cr}$ values of solutions generated during Cr-electroplating, chromating and anodizing at nine industrial sites. The source chemical, CrO_3 , had a mean $\delta^{53}\text{Cr}$ of 0.0 ‰. A small-to-negligible Cr isotope fractionation was observed between the solutions of the plating baths and the source chemical. Across all sample types, the mean $\delta^{53}\text{Cr}(\text{VI})$ value was 0.2 ‰. The mean $\delta^{53}\text{Cr}(\text{VI})$ value of contaminated groundwater in the same region, studied previously, was significantly higher (2.9 ‰), indicating Cr(VI) reduction. Based on low $\delta^{53}\text{Cr}(\text{VI})$ values of plating baths and rinsewaters as potential contamination sources, and their low variability, we suggest that most aquifer $\delta^{53}\text{Cr}(\text{VI})$ values higher than 1.0 ‰ are a result of *in-situ* Cr(VI) reduction.

1. Introduction

Chromium belongs to the most abundant inorganic groundwater contaminants at hazardous waste sites (Nriagu and Niebor, 1988). In the pH range common in shallow aquifers (4.5-8.0), the carcinogenic hexavalent form Cr(VI) is soluble and mobile, while the non-toxic trivalent form Cr(III) is mostly insoluble and immobile (Davis and Olsen, 1995). Time-series of decreasing Cr concentrations in groundwaters, and recently also Cr isotope systematics, have indicated natural attenuation in some contaminated aquifers (Ellis et al., 2002, Blowes, 2002). In the presence of reducing agents, such as Fe(II), S(II) and organic C, and/or suitable microorganisms, Cr(VI) is reduced to Cr(III) and removed from the solution. Cr(VI) reduction is associated with a kinetic isotope fractionation. The product, Cr(III), becomes enriched in the lighter isotope ^{52}Cr , while the residual dissolved Cr(VI) becomes enriched in the heavier isotope ^{53}Cr (Ellis et al., 2002, Sikora et al., 2008, Izbicki et al., 2012, Zink et al., 2010, Kitchen et al., 2012, Basu and Johnson, 2012, Basu et al., 2014). The isotope effects are

caused by different strengths of chemical bonds between the heavy and light isotopes. Snapshot sampling and analysis of the $^{53}\text{Cr}/^{52}\text{Cr}$ isotope ratio of the groundwater (expressed in the $\delta^{53}\text{Cr}$ notation as a ‰ deviation from a standard) provides information on the natural ability of an aquifer to attenuate Cr contamination (Ellis et al., 2002, Wang et al., 2015).

One weakness of isotope assessments of spontaneous Cr(VI) reduction in aquifers has been incomplete knowledge of the initial $\delta^{53}\text{Cr}$ value of the contaminant (Izbicki et al., 2012, Johnson and Bullen, 2004, Novak et al., 2014). At many sites contaminated decades ago, industrial operations have been closed, and the original contaminant is not available for isotope analysis. At recently contaminated sites, facility owners are usually reluctant to provide samples of the contaminant. So far, only eight $\delta^{53}\text{Cr}$ values of contamination sources related to electroplating, chromating or anodizing have been published (Ellis et al., 2002, Berna et al., 2010, Novak et al., 2014).

We sampled Cr-containing technological solutions including electroplating, chromating and anodizing baths at nine industrial sites in the Czech Republic, and analyzed them isotopically. At five of these sites, we obtained also the solid source chemical. Our objective was to define the range of $\delta^{53}\text{Cr}$ values of potential sources of groundwater pollution. We hypothesized that Cr (electro)plating at a variety of industrial sites produces only a narrow range of Cr isotope ratios. If so, future studies could, with a reasonably high degree of confidence, use the $\delta^{53}\text{Cr}$ values determined here to represent the $\delta^{53}\text{Cr}$ values of past contamination from electroplating, chromating, and anodizing industries. Additionally, we compared $\delta^{53}\text{Cr}$ values of plating baths with published $\delta^{53}\text{Cr}$ data on contaminated aquifers from sites that, in the past, used these technologies, and made inferences on *in-situ* Cr(VI) reduction.

2. Materials and methods

2.1. Study sites

Samples for determination of Cr concentration and isotope composition were obtained from nine industrial sites (Fig. 1). At all sites, chromic anhydrite (CrO_3) was used as the **source chemical**. Samples of CrO_3 were obtained from Jilemnice, Hostivar, Nove Mesto nad Metuji,

Dacice, and Zruc nad Sazavou (Tab. 1, and Tab. A1 in the Appendix). **Chromium hard plating** was carried out at five sites (Jilemnice, Hostivar, Nove Mesto nad Metuji, Dacice and Chotebor). **Decorative plating** was performed at three sites (Decin, Chotebor, and Zruc nad Sazavou). Four sites performed **chromating** (Hostivar, Decin, Chotebor, and Letnany). At one site (Letnany), **anodizing bath** was sampled. **Plating rinsewater** prior to neutralization was sampled at six sites (Jilemnice, Hostivar, Decin, Letnany, Dacice, and Zlate Hory). **Neutralized effluent** was collected at two sites (Jilemnice and Decin; Tab. 1). Names that are underlined in Fig. 1 mark sites where we were able to sample solutions from subsequent technological steps, *i.e.*, from higher to lower Cr(VI) concentrations.

2.2. Technological procedures under study

Chromium hard plating. This technique increases corrosion resistance and surface hardness of metal parts (Mandich and Snyder, 2011). The Cr(VI) bath is a mixture of chromium trioxide and sulfuric acid, which serves as a catalyst. CrO₃ prevails over H₂SO₄ in a 250:1 mass ratio. The electrolyte is extremely acidic. The most popular Cr plating bath contains 125 g Cr L⁻¹. The plating temperature is 65 °C. Pb-Sn anodes are immersed in the bath, the metal parts on which Cr(0) is deposited serve as the cathode. The summary reaction of the Cr deposition is

however, a number of poorly understood partial reactions are involved. A cathode film is formed that itself is not reduced to Cr(0). Metallic Cr is deposited from a Cr complex that passes through the cathode film.

Chromium hard plating is known for low cathode efficiency (Mandich and Snyder, 2011, Downing et al., 2000). Only < 30 % of the electric current is used up for the Cr(VI) to Cr(0) reduction. Another 30 % is consumed by Cr(VI) reduction to Cr(III) that remains in the electrolyte. The rest of the current is consumed by reduction reactions producing H₂. Cr(III) is oxidized back to Cr(VI) on the anode and an equilibrium between the large amount of Cr(VI) and a small amount of Cr(III) in the solution is achieved. All studied Cr plating shops work in a continuous mode. CrO₃ is added to the plating vat every 5 days following a 10-20 % depletion in Cr(VI) in the solution.

Decorative Cr plating is applied over Ni plating. The temperature is lower (45 °C), and Cr(VI) concentrations in the electrolyte higher, compared to hard plating. The deposit on the cathode is composed of Cr(0).

Chromating differs from Cr electroplating in that (i) chromic acid is used not as electrolyte but as an oxidizing agent, and (ii) the resulting protective layer contains Cr(VI) and Cr (III) salts, instead of metallic Cr(0) (Dennis and Such, 1972, Downing et al., 2000). Similar to electroplating, a catalyst is necessary, mostly H₂SO₄. The typical CrO₃ concentration in a chromating bath (3 g L⁻¹) is lower, compared to electroplating. Cr(III) is formed by an addition of pyrosulfite according to the equation

Chromic acid anodizing. Aluminium alloys are anodized to facilitate dyeing (Downing et al., 2000). An Al₂O₃ layer is grown by passing direct current through an electrolyte, made up of CrO₃ and H₂SO₄, with the Al object serving as an anode.

Production of rinsewater. Two types of Cr(VI)-contaminated rinsewater are generated, each in a volume similar to the volume of the plating vat (mostly 3 m³). The first batch of rinsewater is recycled into the plating solution, the second less polluted batch is chemically treated and discharged.

Neutralization of the galvanic sludge and rinsewater. Before neutralization, Cr(VI) predominates over Cr(III). Cr(VI) is reduced under low pH with pyrosulfite, and the resulting Cr(III) is precipitated following neutralization with Ca(OH)₂:

The non-toxic precipitate, Cr(OH)₃, is deposited in landfills, while the residual solutions are released to surface waters (Cannio et al., 2011).

2.3. Sampling and chemical analysis

CrO₃ was obtained in a solid form from the plant owner and dissolved in deionized water. Approximately 500 mL of each technological solution were collected, shaken well and a 50 mL subsample was filtered. Total Cr concentration was determined using a quadrupole ICP MS (Thermo X-series) with a detection limit of 0.5 µg Cr L⁻¹. Cr(VI) concentrations higher than 0.01 g L⁻¹ were determined by iodometric titration using starch as indicator. To avoid interference, Fe(II) was removed by an addition of ammonium fluoride. Cr(VI) concentrations between 0.04 mg L⁻¹ and 0.01 g L⁻¹ were determined spectrophotometrically with 1,5-diphenylcarbazide at 545 nm. The reproducibility was 5-10 %.

2.4. Chemical purification and Cr isotope analysis

Technological solutions were processed through anion exchange columns (Bullen, 2007). Sample volume containing 1-2 µg Cr was loaded on a PolyPrep (Biorad) chromatography column filled with 2 mL of pre-conditioned (2x10 mL of 6 N HCl) anion exchange resin (AG-1-X8, 100-200 mesh) (Cadmova and Chrastny, 2015). Matrix cations were eluted with 20 mL of 0.1 N HCl, and the purified Cr fraction was collected in 6 mL of 6 N HCl. Separation yields for Cr(VI) were 90-95 %. Cr(III) was not isotopically analyzed. The purified Cr(VI)-containing sample was then evaporated to almost dryness, and an aliquot of concentrated HNO₃ was added to obtain a 2 % HNO₃ solution. The evaporation step was repeated twice. Double-spike solutions were prepared from single spikes of ⁵⁰Cr and ⁵⁴Cr (Isoflex, USA) enriched to 99.0 and 99.5 %, respectively. Because our single spikes were differently enriched, and the ⁵⁴Cr spike contained more 'sample' ⁵³Cr, we adjusted the composition of the double spike, so that the ⁵⁰Cr/⁵⁴Cr ratio was 1.494. The optimum sample/spike ratio (R_{opt}) was estimated using the following relationship:

$$R_{\text{opt}} = [(a_{\text{sk}}/a_{\text{si}})(a_{\text{tk}}/a_{\text{ti}})]^{1/2} = (R_{\text{s}}R_{\text{t}})^{1/2}$$

where a is an atomic abundance, s is an unspiked sample, t is an isotope tracer (spike), k is the major isotope in the tracer, i is the major isotope in the sample, and R is a ratio. The optimum sample/spike ⁵⁰Cr/⁵²Cr ratio was then close to unity. The ⁵⁰Cr/⁵⁴Cr double-spike solution was added to the sample prior to analysis (Farkas et al., 2013). We processed the NIST-979 standard through the column in each sample set and did not find any Cr isotope fractionation.

The procedural blank for the anion-exchange method was negligible (15-20 ng Cr). The Cr isotope measurements were performed on a Neptune Thermo MC-ICP-MS. The MC-ICP-MS was operated in a high-resolution mode. Approximately 100 ppb Cr solution in 2 % HNO₃ were introduced into the plasma using an ARIDUS (Cetac) desolvating nebulizer without N₂. Argon flux was increased to almost 9 L min⁻¹, thus suppressing the ArN isobaric interference. All four Cr ions were collected simultaneously. Each measurement consisted of 40 cycles, with a 4-seconds signal integration. A blank measurement was collected between each sample and standard (NIST-979); the standard was analyzed every three samples (Sillero et al., 2014). The raw ⁵⁰Cr/⁵²Cr, ⁵³Cr/⁵²Cr, and ⁵⁴Cr/⁵²Cr data were transferred to a spreadsheet, and instrumental discrimination and natural isotope composition were extracted mathematically using a nested-iteration double-spike calculation. The results were expressed in the δ notation:

$$\delta^{53}\text{Cr} = \left[\left(\frac{{}^{53}\text{Cr}/{}^{52}\text{Cr}_{\text{measured}}}{{}^{53}\text{Cr}/{}^{52}\text{Cr}_{\text{standard}}} \right) - 1 \right] \times 1000 \text{ ‰}.$$

The reproducibility of our $\delta^{53}\text{Cr}$ measurements was $\pm 0.066 \text{ ‰}$ (2 standard deviations; cf., Farkas et al., 2013).

3. Results

3.1. Chromium concentrations in technological solutions

Electroplating baths had the highest mean Cr_{tot} concentrations (120 g L⁻¹), followed by the Al-anodizing bath (31 g L⁻¹) and chromating baths (3 g L⁻¹; Tab. 1-2). Rinsewater prior to neutralization contained on average 0.3 g Cr_{tot} L⁻¹, which is 400 times less than electroplating baths. Following the neutralization step, the concentration of Cr_{tot} in wastewater decreased on average 20 times.

Cr(VI) formed on average 90 % of total Cr in electroplating baths, and 60 % of total Cr in chromating baths (Tab. 1-2). The remaining Cr was formed by the non-toxic Cr(III). The Cr in Al-anodizing bath was formed purely by Cr(VI). Total Cr in rinsewaters prior to neutralization contained on average 83 % of Cr(VI). The remaining Cr in rinsewaters was represented by non-toxic Cr(III). Cr(VI) in neutralized rinsewater was mostly below the detection limit (Tab. 1-2), while a total mean Cr concentration of 15 mg L⁻¹ was measured.

3.2. $\delta^{53}\text{Cr}$ values of the source chemical

Chromium trioxide (CrO_3) was the source chemical at all studied industrial sites. Its mean $\delta^{53}\text{Cr}$ value was $0.0\text{‰} \pm 0.1$ (SD) (Tab. 2). The range of $\delta^{53}\text{Cr}$ values of the source chemical was mere 0.1‰ , similar to analytical uncertainty (0.07‰).

3.3. $\delta^{53}\text{Cr(VI)}$ values of technological solutions

$\delta^{53}\text{Cr}$ values of all technological solutions spanned 1.3‰ (-0.4 to 0.9‰), indicating higher Cr isotope variability, compared to the source chemical (Tab. 1-2). Both the minimum and the maximum $\delta^{53}\text{Cr}$ values were found at a single site, Decin. The mean $\delta^{53}\text{Cr}$ value of all technological solutions, including rinsewaters, was $0.2\text{‰} \pm 0.3$. Most $\delta^{53}\text{Cr}$ values of technological solutions were close to 0.0‰ , *i.e.*, to the mean $\delta^{53}\text{Cr}$ value of the source chemical.

The mean $\delta^{53}\text{Cr}$ value of the hard + decorative electroplating baths was $0.2\text{‰} \pm 0.2$. The mean $\delta^{53}\text{Cr}$ value of the chromating baths was 0.3‰ . Chromium in rinsewaters following neutralization (0.4‰) was isotopically slightly heavier than Cr in rinsewaters prior to neutralization (0.1‰). The $\delta^{53}\text{Cr}$ value of the Al-anodizing bath was -0.1‰ .

3.5. Time-series of Cr concentrations and $\delta^{53}\text{Cr}$ values of technological solutions

At Jilemnice and Decin, Cr(VI) concentrations decreased from the plating bath to the rinsewater to the neutralized effluent (Fig. 2, solid circles). This decrease, however, was not accompanied by any systematic trend in $\delta^{53}\text{Cr(VI)}$ (Fig. 2, open circles).

4. Discussion

4.1. The source chemical

The Cr isotope composition of the source chemical was practically identical to the Cr isotope composition of the Earth's mantle and chromite deposits: The mean $\delta^{53}\text{Cr}$ value of CrO_3 used in Czech electroplating/chromating baths was 0.0‰ , while the mean $\delta^{53}\text{Cr}$ value of mantle-

derived rocks is -0.124 (Schoenberg et al., 2008), and $\delta^{53}\text{Cr}$ of world chromites is -0.079 ‰ (Farkas et al., 2013). Because the smelting process proceeds at high temperatures (1600 °C), Cr isotope fractionation is unlikely (Schoenberg et al., 2008). The recovery of Cr(VI) during the production of chemicals is close to 100 %, and hence only negligible change in the isotope composition of the Cr(VI) pool is expected. The largest range of $\delta^{53}\text{Cr}$ values of highly purified commercial chemicals was reported by Schoenberg et al. (2008) as -0.44 to 0.02 ‰. Our source chemical, CrO_3 , did not undergo multi-step purification and had a much narrower range of $\delta^{53}\text{Cr}$ values.

4.2. Should an isotope fractionation be expected in Cr plating baths?

Black et al. (2014) summarized stable isotope fractionations accompanying electroplating of three transitional metals (Fe, Zn, and Cu), and one alkali metal (Li) (Kavner et al., 2005, 2008, 2009, Black et al., 2009, 2010a, 2010b, 2011). Light stable isotopes of all these metals were preferentially electroplated, and the difference between δ values of the reactant and the product was large, mostly 2 to 5 ‰ (Black et al., 2014). In closed-system experiments, the isotopic evolution of the residual stock solution followed Rayleigh distillation of the reservoir. Fractionation decreased with an increasing rate of metal deposition, and increased with the stirring rate. Maximum observed kinetic fractionations were higher than the predicted equilibrium fractionations (Black et al., 2014).

Theoretical calculations of equilibrium isotope fractionations accompanying the reduction of Cr(VI) were performed by Schauble et al. (2004). The largest equilibrium fractionations up to 7.6 ‰ are associated with the Cr(VI) to Cr(III) reduction. Smaller equilibrium fractionations of 3 ‰ are associated with the Cr(III)-to-Cr(0) reduction. Thus, if the isotope behavior of Cr were similar to the previously studied metals, we would expect a relatively large isotope fractionation associated with Cr electroplating.

4.3. The observed Cr isotope fractionations

The observed kinetic Cr isotope fractionations in plating baths, relative to the source chemical, were small to negligible (Tab. 1-2). Most $\delta^{53}\text{Cr}$ values of plating solutions were close to 0 ‰ which was the isotope signature of the source chemical. Across all reaction types [Cr(VI)-to-Cr(0) reduction in electroplating, Cr(VI)-to-Cr(III) reduction in chromating,

anodizing], and across all sample types (Tab. 1-2), the variability in $\delta^{53}\text{Cr}$ (1.3 ‰) was smaller than both the magnitude of Cr isotope fractionations calculated for equilibrium processes (7.6 ‰) (Schauble et al., 2004), and the magnitude of kinetic abiotic/biotic Cr(VI) reduction measured in the laboratory (2.2-5.4 ‰; Ellis et al., 2002, Sikora et al., 2008, Johnson and Bullen, 2004, Zink et al., 2010, Kitchen et al., 2012. Basu and Johnson, 2012, Basu et al., 2014). Our larger $\delta^{53}\text{Cr}$ data set gives results slightly lower than three previous reports, which were based on several samples only. Ellis et al. (2002) analyzed three plating baths, arriving mean $\delta^{53}\text{Cr}$ value of 0.3 ‰, Novak et al. (2014) analyzed four technological solutions, also arriving at a mean $\delta^{53}\text{Cr}$ value of 0.3 ‰. Berna et al. (2010) analyzed one plating bath (0.8 ‰). All three studies concluded that Cr plating baths appear to be isotopically similar to the source CrO_3 even after several years of use, during which significant amounts of Cr(VI) are consumed by the plating process (Ellis et al., 2002).

From the plating bath to rinsewater to neutralized effluent, the amount of residual Cr(VI) systematically decreases, but only the first and the last process is based on redox reactions where kinetic isotope effects can be expected. The $\delta^{53}\text{Cr}$ trend down the concentration gradient appears to be site-specific (Fig. 2). Only at Decin did the neutralization of the rinsewater result in slightly higher $\delta^{53}\text{Cr}$ value, compared to the values for the plating bath and rinsewater before neutralization. Pilot data in Fig. 2 are based on snapshot sampling. Replicated data are needed to evaluate whether Cr(VI) reduction during neutralization leads to a systematic enrichment in the heavier isotope ^{53}Cr in the residual fraction.

4.4. Why is kinetic Cr isotope effect not expressed during Cr(VI) reduction

Chromium electroplating is a relatively rapid process, taking less than 15 minutes. Such a relatively high reaction rate may result in a small isotope effect (Johnson and Bullen, 2004). Berna et al. (2010) stressed that the bath becomes only slightly enriched in heavier Cr isotopes provided the rate of Cr loss as Cr(0) is small compared to the rate of Cr(VI) replenishment to the bath.

Without exception, the Cr(VI) plating solution is replenished as soon as 10 to 20 % of dissolved Cr have been removed via Cr(0) deposition and loss of solution during operations. Fig. 3 plots the evolution of $\delta^{53}\text{Cr}$ values of the bulk residual Cr(VI) in the plating bath as the reaction proceeds. The graph is based on Rayleigh distillation in a closed system, where $\delta^{53}\text{Cr}$

of the reactant is 0 ‰, and the chosen fractionation factor α of 0.9966 is an experimental value for the Cr(VI)-to-Cr(III) reduction (Ellis et al., 2002). A 10 % consumption of dissolved Cr(VI) before replenishment would lead to a 0.4 ‰ enrichment in the heavier isotope ^{53}Cr in the bath. A 20 % consumption of Cr(VI) would lead to a 0.8 ‰ enrichment in the heavier isotope ^{53}Cr in the bath. The low extent of reaction before Cr(VI) replenishment does not sufficiently explain the small fractionation observed in the remaining Cr(VI) in the bath (0.2 ‰).

The magnitude of fractionation expressed during chemical reaction depends on the inherent isotope effect for the reaction, and mass transport limitation (Kavner et al., 2005, 2008, 2009, Black et al., 2009, 2010a, 2010b, 2011, 2014). Under mass-transport limited conditions, the chemical reaction takes place more quickly than the reactant can be replaced. Black et al. (2014) concluded for Fe, Zn and Cu that at least two competing processes determine the isotope fractionation during electroplating. One example is competition between mass transport and electrochemical kinetics (Black et al., 2014). For Cr electroplating, Johnson and Bullen (2004) suggested that the small-to-negligible isotope fractionation results from its multi-step nature. Cr(VI) migrates across an electric field gradient with little back-reaction. The $\delta^{53}\text{Cr}$ value of Cr removed from the solution is close to that of the bulk solution, despite the kinetic isotope effect occurring during the Cr(VI) reduction step itself. We note that during Cr hard plating and decorative plating, a small amount of Cr(III) which resulted from Cr(VI) reduction is oxidized on the anode back to Cr(VI) (Greenwood, 1964, Dennis and Such, 1972). This process further complicates the explanation of the overall Cr isotope effect. Controlled Cr electroplating experiments are needed as the next step.

No previous laboratory isotope studies focused on chromating which uses CrO_3 not as an electrolyte but as an oxidizing agent. Chromating is similar to Cr electroplating in that (i) some Cr(VI) is reduced to Cr (III), and (ii) both these Cr species co-exist in the bath. Isotope effects of Cr electroplating and chromating are similarly small, but experimental work is needed to obtain an insight into the exact mechanisms.

4.5. Comparison between $\delta^{53}\text{Cr}$ values of technological solutions and polluted groundwaters

Fig. 4 shows $\delta^{53}\text{Cr}$ histograms of electroplating + chromating baths (a), and rinsewaters (b) based on this study. Data in panel (c) represent six industrial sites (small solid circles in Fig. 1) where leakage of plating baths into aquifers occurred in the past (Novak et al., 2014).

While $\delta^{53}\text{Cr}$ values of plating/chromating baths were statistically indistinguishable from $\delta^{53}\text{Cr}$ values of combined rinsewaters ($p > 0.05$), all technological solutions (a, b) were significantly different from $\delta^{53}\text{Cr}$ values of the six polluted aquifers (c) ($p < 0.001$). The mean $\delta^{53}\text{Cr}$ value of dissolved Cr(VI) in polluted aquifers (2.9 ‰) was 2.7 ‰ higher than the mean $\delta^{53}\text{Cr}$ value of the technological solutions (0.2 ‰; Fig. 4). The same systematics were seen at the two sites where $\delta^{53}\text{Cr}$ values of both the pollution source and polluted groundwater were known: At Zlate Hory, the mean $\delta^{53}\text{Cr}$ value of polluted groundwater was 1.6 ‰ (Novak et al., 2014), i.e., 1.7 ‰ higher compared to the technological solution (-0.1 ‰; Tab. 2). At Letnany, the mean $\delta^{53}\text{Cr}$ value of polluted groundwater was 3.9 ‰ (Novak et al., 2014), i.e., 3.3 ‰ higher compared to the technological solution (0.3 ‰; Tab. 2).

4.6. Natural attenuation of Cr(VI) in soils and aquifers in light of low $\delta^{53}\text{Cr}_{\text{source}}$

Above, we have quantified the overall isotope effects of several technological processes using Cr(VI). Spillage of Cr(VI) into the environment can occur at industrial sites using any of these processes. In case of legacy pollution, we do not exactly know, which technology was applied. We suggest that because of the low $\delta^{53}\text{Cr}$ values found for all studied Cr(VI) solutions that contaminate groundwater, identification of spontaneous Cr(VI) reduction in soils, sediments and aquifers becomes more straightforward. There is a general agreement that progressive enrichment in the heavier isotope ^{53}Cr in the residual dissolved Cr(VI) in the contaminated groundwater is a diagnostic feature of spontaneous reduction of Cr(VI) to insoluble Cr(III) (Ellis et al., 2002, Johnson and Bullen, 2004, Sikora et al., 2008, Zink et al., 2010, Kitchen et al., 2012, Wanner et al., 2012, Jamieson-Hanes et al., 2012, Basu et al., 2014, Novak et al., 2014, Economou-Eliopoulos et al., 2014). If, at a particular site, natural attenuation of Cr-contaminated groundwater is documented, costly active remediation might not be needed. This would depend on the efficiency of the natural attenuation, Cr reaction rates vs. groundwater flow rates, the redox capacity of the sediment, and availability of biological reducers. The fractionation factor of spontaneous Cr(VI) reduction in the soil and groundwater depends on the reaction mechanism and rate. Previous work has shown that the Cr(VI) reduction shifts $\delta^{53}\text{Cr}$ of the residual reactant to higher values by 2.2-5.4 ‰ (Ellis et

al., 2002, Sikora et al., 2008, Zink et al., 2010, Kitchen et al., 2012. Basu and Johnson, 2012, Basu et al., 2014). As seen in Fig. 4, the upper limit of $\delta^{53}\text{Cr}$ values of technological solutions (panels *a* and *b*), was lower than the lower limit of $\delta^{53}\text{Cr}$ values of polluted aquifers (panel *c*): there was no overlap in the histograms. This relationship is valid for sites in the Czech Republic summarized in Fig. 1, and can be interpreted as indication of Cr(VI) reduction in the contaminated soils and aquifers. Direct evidence is available at Zlate Hory and Letnany, where $\delta^{53}\text{Cr}$ values of both the industrial contaminant and the groundwater were measured (Tab. 2). A number of studies in other parts of the world also reported $\delta^{53}\text{Cr}$ values of the contaminated aquifers higher than 0.9 ‰, *i.e.*, higher than any directly analyzed Cr(VI)-containing technological solutions (Raddatz et al., 2011, Izbicki et al., 2012, Economou-Eliopoulos et al., 2014, Heikoop et al., 2014). For example, Izbicki et al. (2012) reported $\delta^{53}\text{Cr}$ values of aquifers in the U.S. as high as 4.0 ‰, while contaminated aquifers in central Greece had $\delta^{53}\text{Cr}$ values of 2.0 ‰ (Economou-Eliopoulos et al., 2014). Chromium isotope data presented here corroborate the original interpretations by these authors, invoking Cr(VI) reduction in soil and groundwater. We note that interpretation of the Cr isotope signatures in groundwater may be complicated by isotopically selective sorption, precipitation and biological uptake of Cr. Chromium isotope effects associated with sorption were shown to be small by Ellis et al. (2004).

Spontaneous Cr(VI) reduction in groundwater is associated with a larger Cr isotope effect than the reduction of Cr(VI) during electroplating. The slower process of the two is more isotopically selective.

At abandoned sites it is often unclear whether Cr(VI) in groundwater originated from plating baths or rinsewater. As seen in Fig. 5, residual Cr(VI) concentrations in rinsewater following neutralization can be higher than Cr(VI) concentrations in most contaminated aquifers (Novak et al., 2014). On average, Cr(VI) in rinsewater following neutralization had slightly higher $\delta^{53}\text{Cr}$ values (0.4 ‰, Tab. 2) than plating baths and rinsewater prior to neutralization. These slightly elevated $\delta^{53}\text{Cr}$ values, however, are still consistent with our general finding of isotopically lighter Cr in industrial pollution sources, compared to aquifers where spontaneous Cr(VI) reduction is under way.

Our data (Tab. 1) indicate that $\delta^{53}\text{Cr}$ values at industrial sites cannot be efficiently used for source apportionment, *i.e.*, to distinguish between two pollution sources resulting from

electroplating, chromating and anodizing. This is due to a high degree of uniformity in $\delta^{53}\text{Cr}$ values of these contamination sources. By contrast, other pollution sources, such as Cr ore piles, or ultramafic rocks, may produce a wider range of $\delta^{53}\text{Cr}$ values (Izbicki et al., 2012, Frei et al., 2014, Novak et al., 2014). Isotope selectivity of tanning procedures using Cr(VI) could not be investigated. At the time of our study, all tanneries in the Czech Republic used non-toxic Cr(III) chemicals, mostly $\text{Cr}(\text{OH})\text{SO}_4$, instead of Cr(VI) chemicals used several decades ago.

5. Conclusions

Reduction of toxic Cr(VI) to non-toxic Cr(III) is associated with a kinetic isotope fractionation leading to a lower $\delta^{53}\text{Cr}$ value of the product and a higher $\delta^{53}\text{Cr}$ value of the remaining reactant. The $\delta^{53}\text{Cr}$ value of the product, Cr(III) is usually 3 to 4 ‰ lower than the $\delta^{53}\text{Cr}$ value of the reactant, Cr(VI). This effect is used in identification of natural attenuation of Cr(VI)-contaminated aquifers at industrial sites. Several studies reported $\delta^{53}\text{Cr}$ values of aquifer Cr(VI) as high as 6 ‰. Technical Cr produced from chromite ore has a $\delta^{53}\text{Cr}$ value close to the well-constrained isotope signature of Cr deposits, and also the Earth's mantle (-0.1 to 0.0 ‰). Until recently, it was unclear to what extent industrial processes themselves fractionate Cr isotopes so that Cr(VI) leaking into groundwater may bring an already elevated $\delta^{53}\text{Cr}$ signature. In such cases, the high $\delta^{53}\text{Cr}$ value of aquifer Cr(VI) would not necessarily mean occurrence of spontaneous Cr(VI) reduction. Data presented here attempt to fill this gap. Based on $\delta^{53}\text{Cr}$ data from nine industrial sites and six types of Cr(VI)-containing technological solutions (hard-plating, decorative-plating, chromating, and anodizing baths, plating rinsewater and neutralized effluent), we have shown that the Cr isotope selectivity of these industrial processes is low. All Cr isotope fractionations accompanying these processes produce potential contaminants with a $\delta^{53}\text{Cr}$ value lower than 1.0 ‰. It is likely that contaminated aquifers in the vicinity of these industrial sites with $\delta^{53}\text{Cr}$ values higher than 1.0 ‰ have experienced removal of Cr(VI) toxicity *via* spontaneous Cr reduction.

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Figure legend:

Fig. 1. Location of sites where technological solutions were collected (large circles; this study), and of Cr(VI)-contaminated aquifers (small circles; data from [8]). 1 – Hradek, 2 – site B (anonymized upon request by owner), 3 – Letnany, 4 – Zlate Hory, 5 – Loučna, 6 – Bruntal.

Fig. 2. Cr(VI) concentration and Cr isotope composition for three different solutions at two sites. Decreasing Cr(VI) concentrations during a sequence of technological processes is not always accompanied by an increasing $\delta^{53}\text{Cr}$ of the residual Cr(VI).

Fig. 3. Rayleigh distillation plot for a closed-system Cr(VI)-to-Cr(III) reduction, assuming $\delta^{53}\text{Cr}(\text{VI})$ of the contamination source of 0.0 ‰ (Tab. 1), and fractionation factor α of 0.9966 (Ellis et al., 2002). A 20 % conversion of Cr(VI) to Cr(III) would result in a 0.8 ‰ enrichment in ^{53}Cr , which is too high, when compared with Cr(VI) reduction during Cr electroplating. Up arrows mark the known 10 to 20 % extent of Cr(VI) reduction before CrO_3 replenishment, left arrows point at the residual $\delta^{53}\text{Cr}(\text{VI})$.

Fig. 4. Histograms of $\delta^{53}\text{Cr}_{\text{Cr(VI)}}$ values of technological solutions (*a* – Cr electroplating baths, chromating baths, anodizing baths; *b* – rinsewaters prior to and following neutralization), and of Cr contaminated groundwater in the Czech Republic (*c*). Groundwater data are from Novak et al. (2014). Different letters (*x*, *y*) mark significantly different values at the 0.001 probability level.

Fig. 5. A comparison of total Cr concentrations in polluted groundwater typical of the Czech Republic (Novak et al., 2014), and total Cr containing technological solutions (this study). Total Cr in rinsewater was enough concentrated to contaminate the aquifers.

Table 1. Chromium concentrations and $\delta^{53}\text{Cr}$ values during (electro)plating (Czech Republic).

611

612 **Table 2.** Summary statistics for total Cr concentration, hexavalent Cr concentration and $\delta^{53}\text{Cr}$
613 values of individual sample types.

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616 **Electronic Appendix:**

617

618 **Table A1.** An overview of Cr sampling. Sample types(s) obtained at each particular site are
619 marked with a solid dot.

620

621

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Table 1. Chromium concentrations and $\delta^{53}\text{Cr}$ values in (electro)plating operations (Czech Republic).

Site	Cr form	Sample type	Description	pH	[Cr tot] (g L ⁻¹)	[Cr (VI)] (g L ⁻¹)	$\delta^{53}\text{Cr} \pm \text{SE}$ (‰)
Jilemnice	CrO ₃	source chemical (Turkey)	dark-purple solid				0.1 ± 0.01
	Cr(VI) solution	hard plating bath	continuous operation for 6 years	< 1.00	130	120	0.1 ± 0.00
	Cr(VI) solution	hard plating bath	continuous operation for 30 years	< 1.00	139	117	0.5 ± 0.03
	residual Cr(VI) + Cr(III) solution	hard plating rinsewater	prior to neutralization	2.57	0.80	0.75	0.8 ± 0.01
	neutralized residual Cr solution	effluent discharging to a brook	following neutralization	7.77	0.01	0.0008	-0.1 ± 0.02
Hostivar	CrO ₃	source chemical	dark-purple solid				0.0 ± 0.02
	Cr(VI) solution	hard plating bath	continuous operation	< 1.00	101	92.8	0.1 ± 0.02
	Cr(VI) solution	hard plating bath	continuous operation	1.82	1.90	1.90	0.1 ± 0.01
	Cr(VI) + Cr(III) solution	chromating bath	continuous operation	2.41	4.12	< 0.01	-0.1 ± 0.06
	Cr(VI) + Cr(III) solution	chromating bath	continuous operation	2.35	1.45	< 0.01	0.0 ± 0.03
	residual Cr(VI) + Cr(III) solution	hard plating rinsewater	following neutralization	12.0	0.02	< 0.00004	0.1 ± 0.07
Decin	Cr(VI) solution	decorative plating bath	continuous operation	< 1.00	156	139	0.3 ± 0.02
	Cr(VI) + Cr(III) solution	chromating bath	continuous operation	2.02	1.38	1.32	0.5 ± 0.00
	residual Cr(VI) + Cr(III) solution	rinsewater	prior to neutralization	2.42	0.02	< 0.00004	-0.4 ± 0.01
	neutralized residual Cr solution	effluent discharging to a brook	following neutralization	8.43	0.01	< 0.00004	0.9 ± 0.07

Site	Cr form	Sample type	Description	pH	[Cr tot] (g L ⁻¹)	[Cr (VI)] (g L ⁻¹)	δ ⁵³ Cr ± SE (‰)
Chotebor	Cr(VI) solution	hard plating bath	continuous operation	< 1.00	162	145	0.5 ± 0.01
	Cr(VI) solution	decorative plating bath	continuous operation	< 1.00	140	127	0.1 ± 0.00
	Cr(VI) + Cr(III) solution	chromating bath	continuous operation	1.86	1.94	1.94	0.0 ± 0.01
Nove Mesto nad Metuji	CrO ₃	source chemical	dark-purple solid				0.0 ± 0.03
	Cr(VI) solution	hard plating bath	continuous operation	< 1.00	110	100	-0.1 ± 0.01
Letnany	Cr(VI) + Cr(III) solution	anodizing bath (formation of Al ₂ O ₃ coating)	continuous operation	< 1.00	30.6	30.6	-0.1 ± 0.03
	Cr(VI) + Cr(III) solution	chromating bath	continuous operation	1.81	3.37	3.29	0.9 ± 0.06
	residual Cr(VI) + Cr(III) solution	hard plating rinsewater	following neutralization	8.21	0.01	< 0.00004	0.2 ± 0.05
Dacice	CrO ₃	source chemical	dark-purple solid				0.0 ± 0.01
	Cr(VI) solution	hard plating bath	continuous operation	< 1.00	137	122	0.4 ± 0.09
	residual Cr(VI) + Cr(III) solution	hard plating rinsewater	prior to neutralization	3.33	0.07	< 0.00004	0.0 ± 0.01
Zruc nad Sazavou	CrO ₃	source chemical	dark-purple solid				0.0 ± 0.02
	Cr(VI) solution	decorative plating bath	continuous operation	< 1.00	123	117	0.3 ± 0.03

Site	Cr form	Sample type	Description	pH	[Cr tot] (g L ⁻¹)	[Cr (VI)] (g L ⁻¹)	$\delta^{53}\text{Cr} \pm \text{SE}$ (‰)
Zlate Hory	residual Cr(VI) + Cr(III) solution	hard plating rinsewater	prior to neutralization	n.d.	0.28	n.d.	-0.1

n.d. – not determined

Table 2. Summary statistics for total Cr concentration, hexavalent Cr concentration and $\delta^{53}\text{Cr}$ values of individual sample types.

Sample type	[Cr _{tot}] (g L ⁻¹)			[Cr (VI)] (g L ⁻¹)			$\delta^{53}\text{Cr}$ (‰)		
	Mean $\pm$ SE*	Median	IQR**	Mean $\pm$ SE*	Median	IQR**	Mean $\pm$ SE*	Median	IQR**
CrO ₃							0.0 $\pm$ 0.02	0.02	0.08
hard + decorative plating bath	120 $\pm$ 14.4	134	26.5	108 $\pm$ 12.8	118.5	21.5	0.2 $\pm$ 0.06	0.18	0.28
chromating bath	2.73 $\pm$ 0.80	1.94	2.33	1.66 $\pm$ 0.733	1.320	2.62	0.3 $\pm$ 0.18	0.04	0.49
rinsewater prior to neutralization	0.30 $\pm$ 0.25	0.175	0.353	0.25 $\pm$ 0.250	0.000	0.375	0.1 $\pm$ 0.26	-0.04	0.38
rinsewater following neutralization	0.015 $\pm$ 0.005	0.015	0.005	<0.00004			0.4 $\pm$ 0.22	0.40	0.20
anodizing bath	30.6***			30.6			-0.1		
polluted groundwater from Figure 2	0.005 $\pm$ 0.003	0.001	0.002	0.005 $\pm$ 0.005	0.001	0.002	2.9 $\pm$ 0.16	2.80	1.21

*standard error

**inter-quartile range

***one value available

Table A1. Cr sampling scheme. • - sample(s) obtained.

Site	Company	Type of Cr samples							
		So ur ce ch em ica l*	Ha rd pla tin g ba th	De cor ati ve pla tin g bat h	Ch ro ma tin g bat h	Pla tin rin se wa ter	An odi zin g bat h	Le at he r nn ing	Ne ut ral ize d eff lue nt
Jilemnice	MZ-chrom	•	•			•			•
Hostivar	TK Galvanoservis	•	•		•	•			
Decin	Denas			•	•	•			•
Chotebor	Galvanovna, s r.o.		•	•	•				
Nove Mesto nad Metuji	Repon	•	•						
Letnany	Letov/LATECOERE				•	•	•		
Dacice	Federal Mogul Valvetrain	•	•			•			
Zruc nad Sazavou	Wikov Sazavan	•		•					
Zlate Hory	Velobel					•			

*CrO₃ for all technologies