



## **Chromium isotope inventory of Cr(VI)-polluted groundwaters at four industrial sites in Central Europe**

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Chromium is one of the most toxic elements, especially in its dissolved Cr(VI) form. In the Czech Republic (Central Europe), massive contamination of groundwater has been reported at more than 200 industrial operations. Under suitable conditions, i.e. low Eh, and high availability of reductive agents, Cr(VI) in groundwater may be spontaneously reduced to solid, largely non-toxic Cr(III). This process is associated with a Cr isotope fractionation, with the residual liquid Cr(VI) becoming enriched in the heavier isotope  $^{53}\text{Cr}$ . At industrial operations that have been closed and/or where no further leakage of Cr(VI) occurs, the contaminated groundwater plume may be viewed as a closed system. At such sites, an increasing degree of Cr(VI) reduction should result in an increasing  $\delta^{53/52}\text{Cr}$  value of the residual liquid. Here we present  $\delta^{53/52}\text{Cr}$  systematics at four contaminated Czech sites, focusing on groundwaters. At two of the four sites (Zlate Hory, Loucna) we were also able to analyze the source of contamination. Chromium in the electroplating solutes was isotopically relatively light, with  $\delta^{53/52}\text{Cr}$  values  $<1$  per mil. At the remaining two sites (Letnany and Velesin), the Cr isotope signature of the source of contamination was not known. At all four sites, most  $\delta^{53/52}\text{Cr}$  values were positive, with means higher than 1 per mil: At Zlate Hory,  $\delta^{53/52}\text{Cr}$  ranged between  $-2.2$  and  $+3.0$  per mil (mean of  $+1.5$  per mil); at Loucna,  $\delta^{53/52}\text{Cr}$  ranged between  $0$  and  $+4.0$  per mil (mean of  $+1.7$  per mil); at Letnany,  $\delta^{53/52}\text{Cr}$  ranged between  $+2.0$  and  $+4.5$  per mil (mean of  $+3.2$  per mil); and at Velesin,  $\delta^{53/52}\text{Cr}$  ranged between  $+0.5$  and  $+4.5$  per mil (mean of  $+2.7$  per mil). Cr(VI) reduction may proceed at Zlate Hory and Loucna, where  $\delta^{53/52}\text{Cr}(\text{VI})$  values in groundwater were on average higher than those of the contamination source. At these two sites, our Cr isotope data are not consistent with the existing estimates of the amount of dissolved and precipitated Cr: The pool size of solid Cr(III) in the soil was estimated at  $6600$  and  $500$  kg at Zlate Hory and Loucna, respectively. At the same time, the pool size of dissolved Cr(VI) was estimated at  $50$  and  $1.2$  kg at Zlate Hory and Loucna, respectively. It follows that, at both sites, less than 1 % of the entire Cr that had leaked into the aquifer in a liquid form remained in the liquid form. If, indeed, most solid Cr now present in the saturated zone had undergone anaerobic reduction, we would expect much higher  $\delta^{53/52}\text{Cr}$  values of the residual liquid Cr(VI) than those actually observed. Our understanding of the system is incomplete. Currently,  $\delta^{53/52}\text{Cr}$  values of the contaminated soils are being determined in an attempt to close a Cr isotope mass balance.