Assessment of chromate reduction efficiency in a field scale PRB in Thun (Switzerland) by measuring Cr-Isotopes

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In Thun, Switzerland, a PRB for Cr(VI) reduction by iron shavings was installed in spring 2008. The barrier design was the same as used in Willisau, Switzerland, reported previously (Flury, 2009). Both PRBs are composed of a double array of vertical piles containing iron shavings and gravel. The aquifer in Thun is almost saturated with dissolved oxygen and the groundwater flow velocities are ca. 10 m/d. Cr(VI) concentrations still exceed the Swiss threshold value for contaminated sites downstream of the barrier after implementation of the PRB in Thun. By performing column experiments and reactive transport modeling two possible mechanisms explaining the insufficient Cr(VI) reduction were identified (Wanner, 2009): (i) Declining reactivity of the iron shavings due to passivation by crusts of iron oxides/hydroxides and carbonates, and (ii) low permeability of the individual piles of the barrier leading to a bypass of the Cr(VI) plume. Cr-Isotopes are fractionated during the process of Cr(VI) reduction, and the extent of reduction can be quantified using the common mass balance approach of Rayleigh type fractionation processes (Ellis, 2002). Ellis determined a fractionation factor of 3.4%. The result of the fractionation is that remnant dissolved Cr(VI) is isotopically heavier than the source if a part of the Cr(VI) load was reduced by the PRB.

In this study the $\delta^{53}$Cr values of 7 groundwater samples from the site in Thun were determined using the method described by Schoenberg (2008). $\delta^{53}$Cr values of the 4 hotspot samples upstream of the PRB were in the range of 0.633-1.136‰ indicating an isotopically heterogeneous Cr(VI) source. The $\delta^{53}$Cr values of the 3 samples downstream of the PRB were 0.924‰, 1.421‰ and 1.659‰. The sample that did not show an increase in the $\delta^{53}$Cr value compared to the hotspot samples was taken downstream of the edge of the PRB. This missing fractionation was explained by a barrier bypass of the Cr(VI) plume at the edge of the barrier. The increase in the $\delta^{53}$Cr values of the two other downstream samples demonstrates that a part of the Cr(VI) plume is reduced within the PRB. The quantification of the amount of Cr(VI) reduction within the PRB is not possible because the $\delta^{53}$Cr values represent a mixture of a Cr(VI) load that was partially reduced and a Cr(VI) load that was potentially bypassing the barrier. Taking the average $\delta^{53}$Cr value of the hot spot samples (0.867‰) and the average $\delta^{53}$Cr value of the downstream samples (1.54‰), a minimal overall reduction efficiency of approximately 24% was quantified.

Considering the fact that only parts of the Cr(VI) load is reduced by the PRB in Thun we conclude that a complete chromate reduction by PRBs is very difficult to achieve in an almost oxygen saturated aquifer with high groundwater velocities.

References: