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Assessing the remediation of chromate contaminated sites: Laboratory experiments, field studies and reactive transport modeling

Chromate is one of the most common and most serious contaminants among inorganic compounds. It is mostly released by the galvanic industry, the wood preservation industry and from tanneries. Caused by accidents or intentional spills chromate compounds reached or still reach the subsurface, where they form a serious threat for drinking water quality. The behavior of chromate compounds in the environment is strongly controlled by site-specific redox conditions, which are often difficult to quantify. Regarding remediation, various engineering and scientific questions are still unresolved.

This thesis provides a detailed investigation of two chromate contaminated sites, where completely different mineralogical and geological conditions are determining chromate behavior. The main goal was to evaluate the remediation measures that were planned or had already been installed by a complete geochemical process understanding. Beside standard analytical techniques, the recently developed technique of measuring stable Cr isotope ratios was applied to groundwater and for the first time to contaminated subsoil samples in order to track field scale Cr(VI) reduction. A particular effort was made to predict future behavior of the two sites and to interpret the obtained data by reactive transport modeling using the computer code CrunchFlow.

At the first study site, located in Thun (western Switzerland) an "industrial rock" containing highly soluble Cr(VI) compounds forms the current Cr(VI) hotspot and is inducing a groundwater Cr(VI) plume with a maximum Cr(VI) concentration of 4 mg/L. The contamination is contained in a carbonate dominated and almost completely oxidized gravel aquifer where the maximum groundwater velocity is ca. 15 m/d. Since the hotspot is located beneath a building of historical value remediation by excavation was hindered and a permeable reactive barrier (PRB) was installed in 2008.

Prior to PRB installation, batch and column experiments were performed using a series of available gray cast iron shavings that form the reactive material of the PRB. The closed system batch experiments clearly demonstrated that the type with the largest individual shaving sizes and largest spherical carbon inclusions was best qualified for the PRB due to its fast Cr(VI) reduction rate. However, the column experiment run with this type and simulating actual field conditions showed a Cr(VI) breakthrough after 60 days of operation. The breakthrough was explained as a result of a decline of reactivity provoked by a strong passivation by observed iron hydroxides and carbonates. Based on the column experiment a reaction network was proposed describing the observed geochemical processes. Reaction rates of this network were calibrated by successfully modeling the observed Cr(VI) breakthrough curves.

After PRB installation by using the best qualified shaving type, Cr(VI) concentrations measured downstream of the PRB were continuing to exceed the Swiss threshold value for contaminated sites. A series of 2D reactive transport model calculations using the calibrated reaction network revealed that these high Cr(VI) concentrations were induced by a barrier bypass of a part of the Cr(VI) plume. This hypothesis was confirmed by performing an extended tracer experiment using two different fluorescence tracers. The experiment revealed that a significant part of the Cr(VI) load is currently bypassing the barrier at a velocity of 12-16 m/day whereas the part flowing through the barrier is transported at a velocity of 4-6 m/day. Cr(VI) reduction efficiency of the PRB was assessed by measuring shifts in Cr isotope ratios ($\delta^{53/52}Cr_{SRM979}$ values) of groundwater samples taken during two sampling campaigns in 2009 and 2010. With one exception, samples originating from locations downstream of the PRB showed a fractionation towards more positive $\delta^{53/52}Cr_{SRM979}$ values compared to the samples originating from the hotspot. This observation is a clear indication of Cr(VI) reduction induced by the PRB. Furthermore, it is an additional confirmation of the barrier bypass hypothesis since the highest Cr(VI) concentrations were measured at the same location where the absence of Cr isotope fractionation was observed. Temporal variation in $\delta^{53/52}Cr_{SRM979}$ values for specific sample locations were related to a temporally variable overall PRB Cr(VI) reduction efficiency possibly dependent on actual hydrological situation. Using a Rayleigh fractionation model it was demonstrated that the Cr(VI) load flowing through the PRB is reduced to an extent of ca. 90%.

Based on the observation made at the Thun site it is inferred that the key parameter for a successful PRB operation is first of all a proper barrier flow through, to be assured by a sufficiently large permeability. Declining reactivity of gray cast iron shavings as well as pore space clogging induced by precipitating secondary minerals are assumed to form an additional threat to the success of a PRB. In the overall context it is concluded that a complete and long-term Cr(VI) reduction induced by a PRB is extremely difficult to achieve for Cr(VI) contaminations located in nearly oxygen and calcium carbonate saturated aquifers, where high groundwater velocities are observed.

The second case study is located in Rivera in the southern part of Switzerland. Here, the chromate contamination has its origin from the production of chromic acid, which was periodically spilled into the subsurface. The contamination affects a gravel aquifer, which is composed of weathering products of the surrounding Ceneri-Gneiss including known Cr(VI) reducing agents such as Fe^{2+} bearing minerals (magnetite, biotite, chlorite and hornblende). Furthermore, the aquifer contains lenses of fine-grained sediments (silty-sand) with an increased organic carbon content of 1-2 wt%, which also forms a potential Cr(VI) reducing agent.

Using a hot alkaline extraction procedure, a total Cr(VI) contamination of several 1000 kg was estimated. Jarosite, $KFe_3((SO_4)x(CrO_4)1-x)2(OH)_6)$, and chromatite ($CaCrO_4$) were identified as Cr(VI) bearing mineral phases, both limiting groundwater Cr(VI) concentrations. In order to track assumed Cr(VI) reduction at field scale, $\delta^{53/52}Cr_{SRM979}$ values of contaminated subsoil samples in addition to groundwater $\delta^{53/52}Cr_{SRM979}$ data were used. The measurements clearly showed a fractionation of groundwater $\delta^{53/52}Cr_{SRM979}$ values towards positive values and subsoil $\delta^{53/52}Cr_{SRM979}$ towards negative values
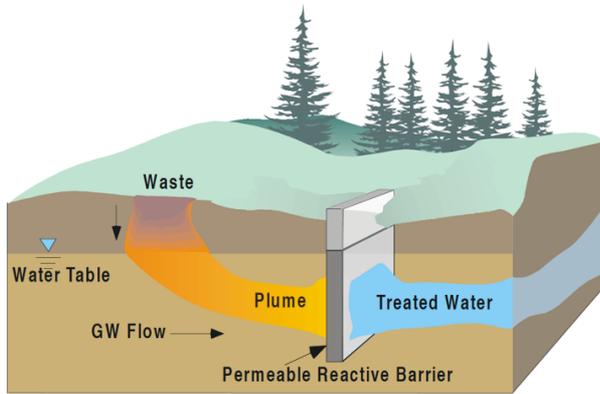
confirming reduction of soluble Cr(VI) to insoluble Cr(III). Using a Rayleigh fractionation model, a current Cr(VI) reduction efficiency of approximately 38% along a flow path of 120 m length was estimated at an average linear groundwater velocity of 3.3 m/d. Groundwater and subsoil $\delta^{53/52}Cr_{SRM979}$ values were compared with a site specific Rayleigh fractionation model, proposing that subsoil $\delta^{53/52}Cr_{SRM979}$ values can possibly be used to track a higher past Cr(VI) reduction efficiency at the time period of industrial activity.

A 2D horizontal reactive transport model of the Rivera site was developed in order to evaluate alternate site remediation strategies. Simulation of the measured present day Cr(VI) plume and $\delta^{53/52}Cr_{SRM979}$ value distribution was used for the 2D model calibration and corresponds to a situation where only monitored natural attenuation (MNA) is occurring. The simulation of alternate excavation scenarios clearly showed that with an excavation of the top 2-4 m the groundwater Cr(VI) plume could be minimized, and that a deeper excavation depth only diminishes 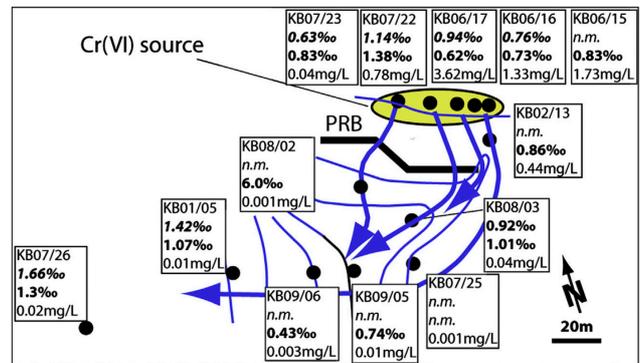the plume further if all the contaminants were re-moved. A combination of an excavation of the top 2-4 m and monitoring of the ongoing Cr(VI) reduction was therefore suggested as the most ecological and economical remediation strategy, even though a remaining time period with ongoing subsoil Cr(VI) contamination in the order of a 1000 years was predicted.

Based on results of the Rivera site it is inferred that at specific (=reducing) subsoil conditions, MNA is a cost-efficient, sustainable and viable remediation strategy for chromate contaminated sites.
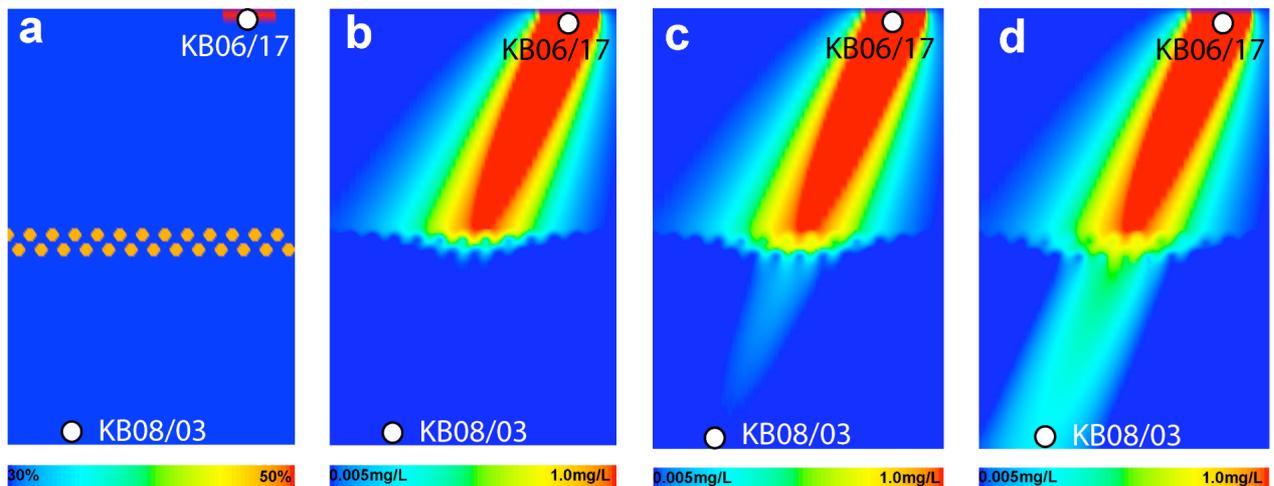
Both case studies improved the general knowledge concerning the behavior of chromate in "quasi natural" and engineered subsurface systems. They clearly demonstrated that when it comes to remediation, a differentiated and site dependent approach is needed. Furthermore, it was shown that a successful remediation is best based on an extended risk assessment using traditional analytical tools in combination with powerful Cr isotope measurements and reactive transport modeling.

Schematic illustration of the principle of a permeable reactive barrier (PRB). PRBs are filled with an appropriate reactive material and are placed perpendicular to a contaminant plume. From Powell et al. (1998)

Spatial distribution of measured Cr(VI) concentrations and $\delta^{53}Cr$ values of samples collected at the Thun PRB site in September 2010. Also shown is the full interpretation of the hydrologic flow field derived from a multi-tracer experiment, Cr isotope measurements and piezometric elevation contour lines obtrained from water table measurements.

Results of model run performed to simulate the theoretical PRB Cr(VI) breakthrough using the reaction kinetics obtained from column experiments (Wanner et al., 2011): a illustrates the model setup in terms of porosity showing the Cr(VI) source area in red, the PRB domain in yellow and the aquifer domain in blue. Obtained temporal Cr(VI) evolution are shown for 100 days (Fig. b), 150 days (Fig. c) and 200 days (Fig. d).