Mineralogical and geochemical characterization of a chromium contamination in an aquifer - A combined analytical and modeling approach

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ABSTRACT

This study presents a detailed mineralogical and chemical characterization of a chromium contamination in alluvial deposits underlying a leather tannery in Austria. Drill cores revealed that the contamination is represented by a black layer that exhibits sharp boundaries with adjacent brown alluvial sediments. This black layer is located below the groundwater table and begins at the source of the contamination. The black layer thickens with increasing distance from the source and the depth of the upper boundary remains at the same level relative to the surface. Mineralogical and chemical investigations showed that the black layer contains reduced Cr phases, a Cr(III) hydroxide and a Cr(III)-Ca-containing hydrocalcite, which are present as discrete grains, in vein-like pore spaces and/or as a coating around mineral grains. Cr(VI) is nearly only present above the groundwater table. Our 2-D model predicts a longitudinal spread of the black layer of approximately 37 m downgradient from the source and a maximum transversal spread of approximately 10 m. This study shows that, if the source of the contamination is not eliminated, the plume will increase continuously farther downgradient.

1. Introduction

Chromium (Cr), a transition metal, has the atomic number 24. According to Rudnick and Gao (2003), it is the 17th most abundant element in the total Earth's crust (upper, middle and lower crust combined). Its known oxidation states range from -2 to $+6$ (Cotton and Wilkinson, 1980). In natural environments, however, the only stable oxidation states are $+3$ and $+6$. Even though it is very rare, elemental Cr does occur naturally (Zhu and Liu, 1981). Chemical and physical properties change depending on the oxidation state, which also affects the impact on the environment and human health. Solid phases containing trivalent chromium (Cr(III)) are relatively insoluble and non-toxic to organisms. In small quantities, Cr(III) is an essential dietary element and is required for sugar and fat metabolism in humans and animals (Anderson, 1997). In contrast, hexavalent chromium (Cr(VI)) is extremely toxic and carcinogenic. Most Cr(VI)-bearing solids are also highly soluble. Although the exact consequences of Cr(VI) and Cr(III) uptake in the human body are still debated, the oral and dermal uptake of Cr(VI) is known to cause chronic and acute health effects and, possibly, death (Costa and Klein, 2008; GESTIS, 2006).

Under oxidizing conditions, Cr(VI) is the most thermodynamically stable redox state of Cr. In water, Cr(VI) occurs as chromate, either as H_2CrO_4 under acidic conditions, or in its deprotonated forms $HCrO_4^-$ and CrO_4^{2-} at higher pH. In natural waters, where the pH typically ranges between 3 and 10, the most abundant species are $HCrO_4^-$ and CrO_4^{2-} (Avudainayagam et al., 2003). The chromate ion dimerizes to dichromate ($Cr_2O_7^{2-}$) at high Cr concentrations in the water (Palmer and Puls, 1996). Chromate is a strong oxidizing agent and is readily reduced in the presence of electron donors such as ferrous iron (Fe^{2+}) or sulfite (SO_3^{2-}) and other ions with a lower reduction potential (Wiberg, 1965). If Cr(VI) is reduced, it will most commonly convert into a trivalent cation or neutral $Cr(OH)_3^0$. Upon changes in pH, Cr(III) ions hydrolyze and polymerize. According to Latimer (1952) and Rai et al. (1987), dissolved Cr(III) forms Cr^{3+} ions as well as $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, $Cr(OH)_4^-$ and $Cr_3(OH)_4^{5+}$ complexes. $Cr(OH)_4^-$ is the only anionic Cr(III) species (Palmer and Wittbrodt, 1991). The predominant species at pH < 4 is Cr^{3+}. At a pH higher than 4, Cr^{3+} hydrolyzes as $Cr(OH)^{2+}$ becomes more stable. The neutral $Cr(OH)_3^0$ species has the widest stability range, from pH 6 to 12 and is therefore the prevailing species in many natural waters. However, predominant speciation can differ from these ideal systems because of the formation of different complexes with other ions in the solution.
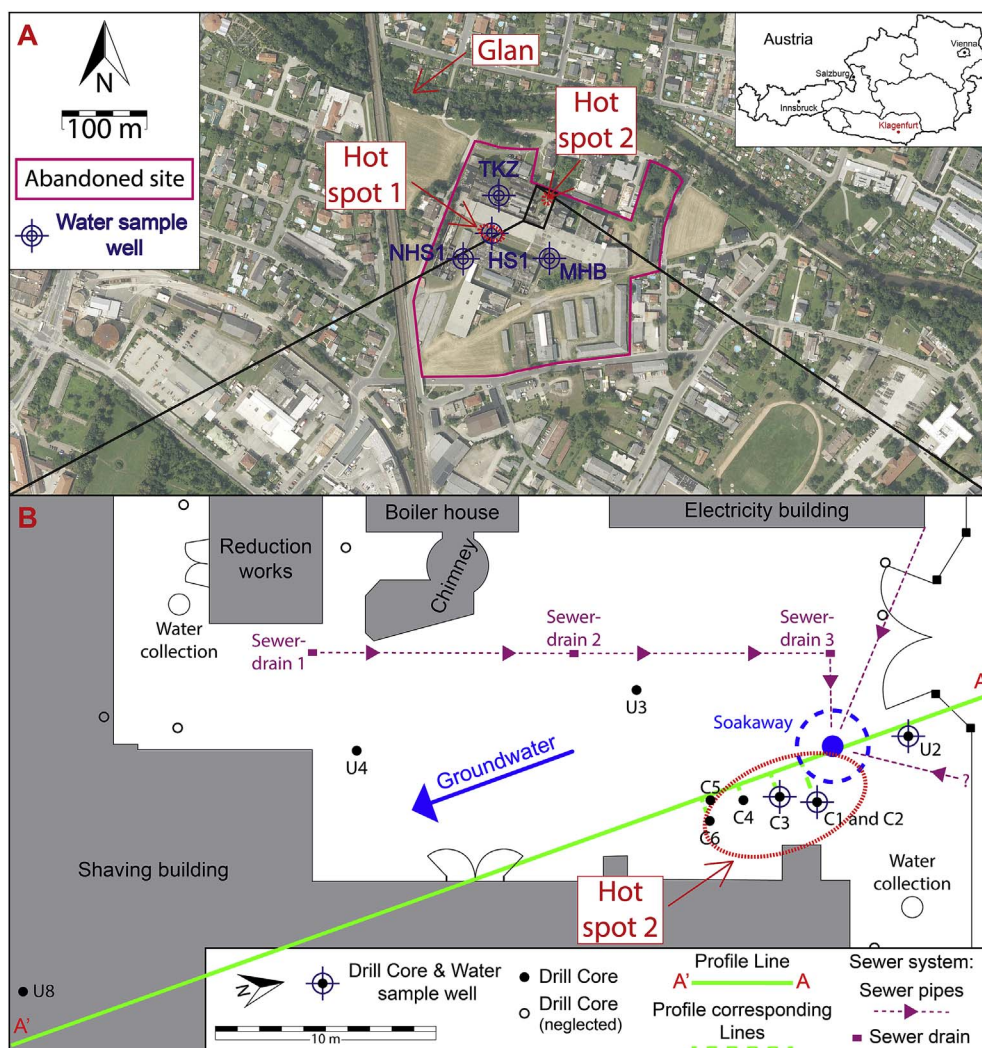
Fig. 1. A: Satellite image from the area northeast of Klagenfurt, marking the abandoned site, groundwater wells where water samples were taken, the study area (the northern part of the contaminated site), the river Glan and the hot spots that were identified (modified from Kagis (2017)). B: Scheme of the northern area of the contaminated site, showing drill core locations (drill cores with black layer identified by C, drill cores without black layer identified by U), groundwater wells, sewer drains and pipes (incl. flow direction), as well as drill sites that are not further considered in this study (modified from Müller et al. (2007)). Groundwater samples presented here were taken from HS1, NHS1, TKZ, MHB, U2, C2 and C3.

Due to its chemical and physical properties, Cr has a wide range of industrial applications, including plating, alloying and tanning. In addition to many further applications, it is used to prevent corrosion by water, as a textile dye and as a pigment (Barceloux and Barceloux, 1999; Petrucci and Harwood, 1993). Spill, leakage, poor storage, improper disposal practices and/or mismanagement in industrial facilities lead to environmental pollution and contaminated sites, which is why a detailed knowledge about the mineralogy and geochemical behavior of Cr in the underground is essential (Calder, 1988; Palmer and Wittbrodt, 1991). The mobility of Cr is controlled by the solubility of the Cr-containing minerals and/or by the adsorption equilibria with specific mineral surfaces or organic materials (Avudainayagam et al., 2003; Chauhan and Sankararamakrishnan, 2011). This mobility has been shown in soils (Bradl, 2004), but it is also relevant in other environmental systems, such as heaps of steel slags (Loncnar et al., 2016).

Thresholds for Cr contamination in groundwater differ from country to country. According to the Austrian risk assessment for contaminated sites (ÖNORM S 2088-1), the threshold for Cr(VI) in groundwater is at 0.01 mg/L, whereas the threshold for further testing in soils is at 50 mg/kg of Cr(tot). Chromium is a common contaminant in the environment and attracts the attention of various researchers, leading to multiple studies on the characterization of Cr contaminations in soils in Europe and elsewhere. Loyaux-Lawniczak et al. (2001), for example, studied the behavior of Cr in soils of a contaminated industrial waste landfill in northern France, and Pawlikowski et al. (2006) described the mineralogy of a Cr contamination, originating from tanning, in river

sediments in Poland. The mobility of Cr, derived from ore processing residues has been investigated and modeled by Geelhoed et al. (2001) suggesting that precipitation and co-precipitation are the controlling processes for the mobility of Cr. Gao and Schulze (2010), characterized Cr-contaminated soil samples and reported Cr contaminations in the soil ranging from 13 up 1562 mg/kg. Földi et al. (2013) reported Cr concentrations up to 109 g/kg in samples of waste and soils affected by the production of Cr tanning agents; by using elemental concentrations to distinguish between waste and soil samples. They concluded, however, that the soil samples were generally depleted in Cr. They further found a positive correlation between Ca and Cr. Qafoku et al. (2010) examined the role of reduction in the transport of Cr in acidic waste-contaminated subsurfaces; their column experiments with samples from the vadose zone showed that surface Cr had been reduced by Fe(II) and that Cr-bearing solids are partially associated with Fe(III). Dresel et al. (2008) published a geochemical description of the chromate hot spot in the vadose zone from the same site. Wanner et al. (2012a; b) published a site characterization as well as a transport model, simulating the natural attenuation. Several of these investigations address Cr-contaminated soils and their implications on the environment, but a detailed mineralogical and geochemical characterization of a Cr hot spot situated in the groundwater, combined with a modeling approach that simulates the plume size, has not yet been published.

In this study, we investigate the origin and extent of a Cr contamination at an abandoned leather tannery in Carinthia, Austria. The focus is on a striking black layer that occurs within water-saturated