



Determination of hexavalent chromium concentrations in matrix porewater from a contaminated aquifer in fractured sedimentary bedrock



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ABSTRACT

A new method for quantification of hexavalent chromium (Cr(VI)) in the porewater of rock core samples from contaminated sedimentary bedrock has been developed here. The method combines alkaline extraction with cation exchange column separation followed by determination of Cr concentrations by inductively coupled plasma mass spectrometry (ICP-MS). A porewater detection limit of 45 µg/L was determined by performing extractions on uncontaminated samples, and accounts for dilution of porewater volumes by the extraction solution. Recoveries of Cr(VI) in quality control (QC) samples were greater than 90% and there was no significant interference from Cr(III). Relative standard deviations (RSD) were less than 10% for QC samples spiked with Cr(VI), and 2 to 47% (average of 21%) for replicate analyses of core samples. Cr(VI) analyses were conducted on depth-discrete core samples collected at intervals of <0.3 m from sandstone and siltstone bedrock within a contaminated groundwater plume. Groundwater samples were collected using multilevel well ports and were also analyzed for Cr(VI) concentrations. Significant Cr(VI) anomalies were observed in the rock matrix of the core samples. Overall, we observe general agreement in the Cr(VI) concentrations between the samples of immobile rock-matrix porewater and the samples of groundwater which is mobile in rock fractures. This method provides a viable procedure for determination of Cr(VI) concentration in bedrock porewater, and these datasets are valuable for developing conceptual models, assessing plume transport and fate, and for considering remedial options.

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1. Introduction

Chromium has two stable oxidation states, trivalent Cr(III) and hexavalent Cr(VI). At low concentration levels, Cr(III) is an essential micronutrient (Anderson, 1997), whereas Cr(VI) is considered a toxin and carcinogen (Barceloux, 1999). Cr(VI) is a contaminant of concern at many contaminated sites, including many Superfund sites (>10%) in the U.S., where in 2011 it was #17 on the Priority List of Hazardous Substances for the Agency for Toxic Substances and Disease Registry (ATSDR, 2013). The US EPA drinking water standard for total chromium is 100 µg/L (USEPA, 2012), and according to the Canadian Drinking

Water Guidelines, the maximum acceptable concentration (MAC) for total chromium is 50 µg/L (Health Canada, 2012). In most naturally occurring minerals chromium is trivalent, such as in the mineral chromite (FeCr₂O₄). In groundwater, Cr(III) is effectively immobile due to its low solubility at near-neutral pH. In contrast, the mobility of Cr(VI) is relatively high when pH is neutral or above, but in neutral to acidic groundwater its mobility is limited by adsorption and reduction to Cr(III) (Nriagu, 1988). Anthropogenic Cr(VI) sources from tank leakage at chrome plating operations, or improper disposal practices are common causes of Cr(VI) contamination in groundwater (Palmer and Wittbrodt, 1991). Knowledge of the physical and chemical-reaction processes affecting Cr(VI) migration in groundwater is required to develop conceptual models and consider possible remediation options (Kent et al., 2007; Palmer and Wittbrodt, 1991). Many studies of Cr(VI) in groundwater indicate that its fate is controlled by the reduction-oxidation of Cr(VI)–Cr(III) (Fantoni et al., 2002; Gray, 2003; Oze et al., 2007), and the transport of Cr(VI) with mobile groundwater in fractured

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porous bedrock is subject to attenuation by diffusion, adsorption and reduction in the rock matrix adjacent to fractures (Fantoni et al., 2002; Friedly et al., 1995). As with other dissolved contaminants, diffusion of Cr(VI) from groundwater flowing in fractures into the immobile porewater within the rock matrix can strongly attenuate plumes in fractured sedimentary rock, but also may cause long-term persistence due to back diffusion and hinder remediation efforts (Parker et al., 2010). Standard groundwater sampling and analytical methods are available to monitor contamination via conventional wells or multilevel monitoring systems. These methods sample groundwater primarily from the fracture networks. To understand the fate and transport of Cr(VI) in fractured porous bedrock, an appropriate sampling and analytical procedure is required for the determination of Cr(VI) concentrations in the matrix porewater where much of the contaminant mass resides at many contaminated sites.

In conducting research into the fate and transport of chlorinated solvents in fractured porous bedrock, Parker et al. (2012) have developed methods using the Discrete Fracture Network (DFN) approach. Utilizing the DFN method, it is possible to quantify the porewater concentrations of volatile organic compounds (VOCs) at contaminated sites, through drilling and extraction of VOCs from rock core samples, allowing for the creation of detailed profiles of contaminant concentrations. Such measurements are integrated into an overall methodology combining matrix sampling and analysis for contaminant concentrations with several other types of borehole measurements and core sample analyses. Our study was motivated by the expectation that application of the DFN approach will improve the understanding of matrix diffusion and reaction processes for Cr(VI) in bedrock porewater, and represents the first DFN application for this contaminant. The conceptual model for Cr(VI) contamination in fractured porous bedrock is shown in Fig. 1,

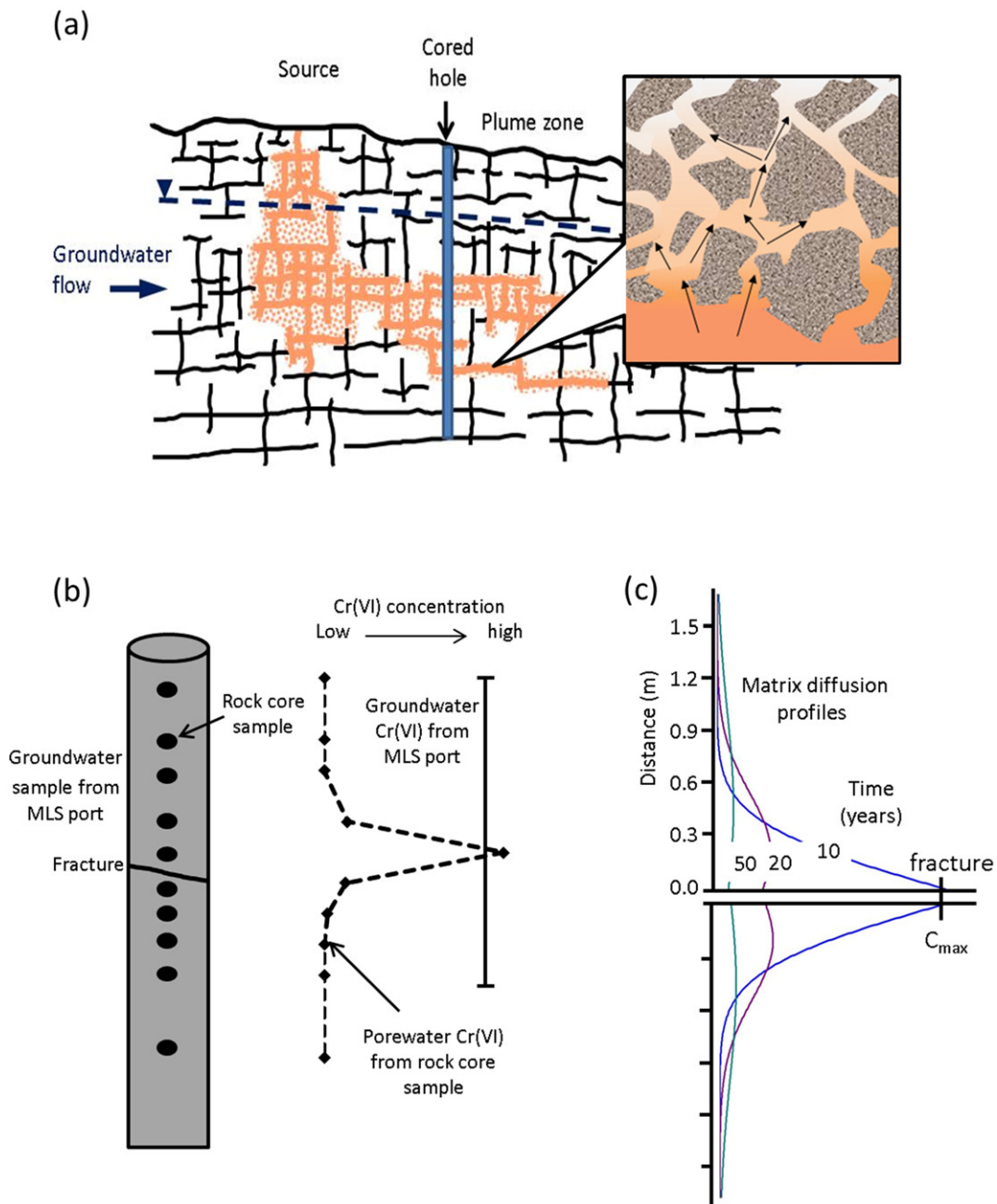


Fig. 1. Schematics of (a) cored hole collected from plume zone for rock core sub-sampling and the diffusion of the Cr(VI) from contaminated groundwater into bedrock matrix, (b) comparison between porewater Cr(VI) from subsampled rock core samples and groundwater Cr(VI) from the sample collected from MLS port and (c) hypothetical Cr(VI) matrix profiles off a fracture for a scenario with a finite source term (declining after 10 years).

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