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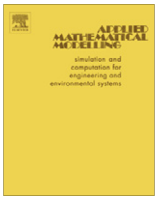

Simulating fate and transport of chromium in saturated sediments

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ABSTRACT

A mathematical model has been developed to improve our understanding of how the transport and bioavailability of chromium are affected by complex sets of microbiological and geochemical reactions. Simulations are performed to illustrate the effect of biotic and abiotic reactions on the fate and distribution of chromium in a saturated sediment and to identify the key process of the reductive transformation of Cr(VI). The results showed that chromium transport and bioavailability could be greatly affected by microbially mediated Cr(VI) reduction. The distribution of chromium in sediments was relatively insensitive to abiotic reaction parameter changes but was sensitive to biotic reaction changes. Because of the finite capacity of biological Cr(VI) reduction, transformation of Cr(VI) into Cr(III) can be most effective in the remediation of chromium contamination under the optimal Cr(VI) concentration and remediation duration.

1. Introduction

Chromium is a ubiquitous contaminant that is widely used in industrial applications such as stainless steel production, leather tanning, metallurgy, and electroplating. The predominant forms of chromium in nature are Cr(III) (trivalent chromium), which mainly presents as chromium aquo-ion ($Cr(H_2O)_6^{3+}$), and Cr(VI) (hexavalent chromium) as chromate ion (CrO_4^{2-}), which have different physicochemical characteristics including mobility, toxicity, and bioavailability [1,2]. Cr(VI) compounds are more soluble and bioavailable in subsurface and aquatic environments than are chromium precipitates composed of Cr(III). The mobile Cr(VI) is, however, a toxic carcinogenic substance that can cause irritation to plants and animals [3,4], whereas the stable Cr(III), an essential nutrient for humans, plays an important role in human glucidic metabolism [5]. The World Health Organization (WHO) reported that chromium is a priority pollutant and proposed a provisional guideline value of 0.050 mg/L for total chromium, mainly soluble Cr(VI), in drinking water [6]. Chromium speciation is significantly affected by ambient redox conditions. Under more oxidizing condition with Eh higher than 0.6 V and pH above 6.0, chromium dominantly remains as Cr(VI), while Cr(III) is stable at pH from 2 to 8 and Eh from +0.295 to −1.0 V [7]. Due to the health risks of Cr(VI), chromium speciation has raised huge environmental concerns, and the transformation of soluble Cr(VI) to insoluble Cr(III) precipitates under reducing conditions is, therefore, an essential step in the remediation of chromium contamination [3].

Reducing agents commonly found in soils include ferrous iron [8], sulfide [9], and organic complexes [10–12]. In addition, iron sulfide is also a very effective reductant for chromium, a prevalent component of reduced soils and sediments that is formed by the reaction of sulfide with iron compounds [13]. It can provide a source of ferrous iron and sulfide and decrease the chance of reoxidation by forming very stable $[Cr,Fe](OH)_2$ solids [3,4,14].

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In addition to the abiotic chemical reduction of Cr(VI), many microorganisms of several genera can utilize Cr(VI) as a terminal electron acceptor during the degradation of organic matters via enzymatic processes and reduce it to Cr(III) under nitrate-reducing conditions [2,15,16]. Experiments under anaerobic conditions showed that Cr(VI) and nitrate were simultaneously used as electron acceptors without preference during degradation processes of organic matter [2]. Microbially mediated Cr(VI) reduction alters toxicity and solubility as well as mobility of this contaminant in subsurface environments.

From the previous researches, it has been known that the Cr(VI) contained in the sediments can be reduced by iron sulfide as well as utilized by native microorganisms as a terminal electron acceptor during organic matter degradation. Although both biotic and abiotic processes have demonstrated the ability to reduce Cr(VI), few studies have focused on both processes simultaneously as conventional methods for Cr(VI) removal. In addition, there were no quantitative analyses between biotic and abiotic processes on the transformation of Cr(VI) to Cr(III) for the remediation of chromium-contaminated sediments. Therefore, it is necessary to develop a mathematical model to improve our understanding of how chromium fate and transport are affected by various biogeochemical and physical processes. The general mathematical framework is based on the effects of complex sets of microbiological and geochemical reactions on chromium transport and bioavailability. Using a series of numerical experiments that apply the proposed model to the immobilization of chromium as Cr(III), the key parameter and its interaction in trace metal bioremediation were identified to provide guidance for further model development and to link model development to ongoing field work.

2. Model development

The fate and transport of trace metals in subsurface environments are closely linked to the biologically mediated redox dynamics in terms of sequential utilization of electron acceptors such as O_2, NO_3^-, Fe(III), and SO_4^{2-} during the degradation of organic carbons [17–19]. Throughout the redox profiles that develop subsurface environments, the fate of trace metals can be directly or indirectly affected via various biogeochemical processes such as reduction/oxidation, sorption/desorption, precipitation/dissolution, and the formation of complex ions as well as physical migration processes such as advection, dispersion, and diffusion.

The model includes mass transport equations for 11 coupled constituents, including solid (organic matter, Fe(III), FeS, and Cr(III)) and dissolved substances (O_2, NO_3^-, NH_4^+, Fe^{2+}, SO_4^{2-}, HS^-, and Cr(VI)), that consider biotic and abiotic reactions. It was assumed that sediments retain a non-limiting source of organic matter from plant litter, root exudates, and root turnover. The biogeochemical reactions included in the model are based on the electron acceptors being utilized by the microorganisms in degrading organic substrates in freshwater sediments and divide the spatial domain of the sediments into four different zones: aerobic respiration, denitrification, iron reduction, and sulfate reduction. The spatial distribution of these zones determines where the chromium is reduced or oxidized, sorbed to different solid phases, and/or precipitated. Their stoichiometric relationships are shown in Table 1. The model outputs consist of vertical concentration profiles of model species and estimates of fluxes of solute substances across the sediment–water interface.

2.1. Mass conservation equations

One-dimensional mass balance equations were formulated for dissolved and solid species of interest in saturated sediments. For each dissolved component (O_2, NO_3^-, NH_4^+, Fe^{2+}, SO_4^{2-}, HS^- and Cr(VI)), a mass continuity equation of an aqueous

Table 1
Stoichiometric relationships among key biogeochemical reactions.

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)+106O_2 \rightarrow 106CO_2 + 16NH_3 + H_3PO_4 + 106H_2O$
$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$
$4Cr(OH)_3 + 3O_2 \rightarrow 4CrO_4^{2-} + 2H_2O + 8H^+$
$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$
$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$FeS + 2O_2 \rightarrow Fe^{2+} + SO_4^{2-}$
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8NO_3^- + 84.8H^+ \rightarrow 106CO_2 + 42.4N_2 + 16NH_3 + H_3PO_4 + 148.4H_2O$
$NO_3^- + 8Fe^{2+} + 21H_2O \rightarrow NH_4^+ + 8Fe(OH)_3 + 14H^+$
$NO_3^- + 4H_2S + 2H^+ \rightarrow NH_4^+ + 4S^0 + 3H_2O$
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 141.3CrO_4^{2-} + 706.5H^+ \rightarrow 106CO_2 + 141.3Cr^{3+} + 16NH_3 + H_3PO_4 + 459.2H_2O$
$8CrO_4^{2-} + 6FeS + 23H_2O \rightarrow 8Cr^{3+} + 6Fe^{2+} + 2S_2O_3{}^{2-} + 22OH^-$
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 424FeOOH + 848H^+ \rightarrow 106CO_2 + 424Fe^{2+} + 16NH_3 + H_3PO_4 + 742H_2O$
$2Fe(OH)_3 + H_2S + 4H^+ \rightarrow 2Fe^{2+} + S^0 + 6H_2O$
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} + 53H^+ \rightarrow 106CO_2 + 53HS^- + 16NH_3 + H_3PO_4 + 106H_2O$
$SO_4^{2-} + CH_4 + 2H^+ \rightarrow H_2S + CO_2 + 2H_2O$
$Fe^{2+} + HS^- \rightarrow FeS + H^+$
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$