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# Leaching and reduction of chromium in soil as affected by soil organic content and plants

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## Abstract

The oxidation state of chromium in contaminated soils is an important indicator of toxicity and potential mobility. Chromium in the hexavalent state is highly toxic and soluble, whereas the trivalent state is much less toxic and relatively insoluble. A laboratory study investigated the impact of growing plants and supplemental organic matter on chromium transport in soil. Plants alone had no appreciable effect on the chromium oxidation state in soil. Soil columns with higher organic content were associated with lower ratios of chromate:total chromium than the columns with lower organic matter. Analyses of column leachate, plant biomass, and soil indicate that more chromium leaching occurred in the vegetated, low organic columns. Retention of Cr in the soils was correlated to the Cr(III) content. Plant uptake of chromium accounted for less than 1% of the chromium removed from the soil. Overall, the addition of organic matter had the strongest influence on chromium mobility.

*Keywords:* Heavy metals; Soil; Chromium; Plants; Rhizosphere; Phytoremediation; Adsorption; Redox; Transport; Leachate

## 1. Introduction

Chromium is used in the electroplating industry as anticorrosive and antibiofoulant agents, and also in steel production and automobile manufacturing. Chromium often occurs in the trivalent (+3, chromic) or hexavalent (+6, chromate) states under natural environmental conditions. The hexavalent state of chromium, Cr(VI), is highly toxic and a human mutagen. The high aqueous solubility of Cr(VI) is of public health concern since the anionic forms, chromate and dichromate, are considered hazardous. The trivalent state of chromium, Cr(III), is much less toxic than Cr(VI). The relative insolubility of Cr(III) results in a reduced threat to water supplies (Kimbrough et al., 1999). The maximum concentration of chromium allowed in drinking water is 0.10 mg/l due to the toxic effects of Cr(VI) and the potential for oxidation of Cr(III) to Cr(VI) (USEPA, 1974).

Soil composition (electron donor availability, soil texture, competing ions, adsorption capabilities, etc.) and conditions in the soil (pH, moisture content, temperature, and the presence of vegetation) are the principal factors affecting the mobility of chromium (Zachara et al., 1989; Hanson et al., 1993; James, 1994; Milacic

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and Stupar, 1995; Chen and Hao, 1996). Chromate ($CrO_4^{2-}$), bichromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$) are weakly sorbed to soils under alkaline to slightly acidic conditions leading to high mobility in the subsurface (Wittbrodt and Palmer, 1995). The presence of other anions in soil reduces potential adsorption sites, resulting in increased mobility of chromate. Chromate mobility is enhanced in neutral pH groundwater, especially in the presence of competing oxyanions (Zachara et al., 1987).

Trivalent chromium is much less mobile and precipitates readily as $Cr(OH)_3$ or $Fe_xCr_{1-x}(OH)_3$ under alkaline to slightly acidic conditions in soil leading to immobility in the subsurface (Wittbrodt and Palmer, 1995). Reduction of Cr(VI) to Cr(III) is an effective means of immobilization and can be induced by inorganic, organic, or biological agents. The predominant chemical reactions in aqueous solutions and soils for chromium are hydrolysis, oxidation, reduction, and precipitation. Hexavalent chromium exists in water only as neutral ($H_2CrO_4^0$) or anionic species ($CrO_4^-$, $CrO_4^{2-}$) (Imai and Gloyna, 1990). Trivalent chromium and water form an octahedral free ion $[Cr(H_2O)_6^{3+}]$, which hydrolyzes to form mononuclear hydroxyl complexes.

Oxidation and reduction reactions are important in the fate, transport, and toxicity of chromium and are more prevalent in soils than groundwater (Barcelona and Holm, 1991). Chromium redox reactions are governed by many factors including aeration; soil moisture content; wetting and drying; iron and manganese status; microbial activity; organic matter; pH; and availability of electron donors and acceptors. Reducing conditions and the formation of Cr(III) are favored as soil moisture content increases, and redox remains low until the water is drained from the soil profile (Masscheleyen et al., 1992).

Manganese oxides have high surface areas and high cation exchange capacities and act as strong scavengers for heavy metals such as chromium (Bartlett, 1991; Kim and Dixon, 2002; Weaver and Hochella, 2003; Stepniewska et al., 2004). Chromium(III) oxidation in soil increases with Mn(IV) oxides content of the soil (Kim and Dixon, 2002). Wetting and drying of soils can induce reduced conditions because of enhanced solubility and lability of organic matter (Bartlett, 1991).

Organic matter has been observed to reduce Cr(VI) in soils (Eary and Rai, 1991; Sharma and Forster, 1993; Anderson et al., 1994; Kozuh et al., 2000; Bolan et al., 2003). Non-humic organic substances such as carbohydrates and proteins also reduce Cr(VI) (Bolan and Thiagarajan, 2001). Adsorption of chromium significantly affects transport of chromium in soil and groundwater. Mineral surfaces with protonated, positively charged sites, particularly iron and aluminum oxides, may adsorb $CrO_4^{2-}$ at pH 2–7 (Zachara et al., 1987). Despite this strong adsorption affinity, chromate is mobile in soil because other competing anions reduce adsorption. Elevated concentrations of $SO_4^{2-}$, $H_4SiO_4^0$, and $HCO_3^-$ may dramatically reduce chromate adsorption in soils. Adsorption of Cr(VI) on hydrous metals oxides decreases with increasing pH; as a result, chromium is often mobile in neutral groundwater environments (Zachara et al., 1989).

Research focusing on the interaction between plants and chromium in rhizosphere soil is relatively limited (Cary and Kubota, 1990; Chang et al., 1992; Bisnoi et al., 1993; Corradi et al., 1993; Han et al., 2004; Weis and Weis, 2004). However, environmental conditions in the rhizosphere may provide information about the potential impact of plant roots on chromium mobility (Chen and Cutright, 2003; Zayed and Terry, 2003). The presence of root exudates may enhance reducing conditions in the soil, which may effectively immobilize chromium (Srivastava et al., 1999). On the other hand, plant roots may release complexing agents, facilitating the uptake of chromium into the plant shoots or increasing Cr mobility in soil. The carboxylic acids and amino acids in root exudates may enhance plant uptake of chromium (Mishra et al., 1996). Once assimilated by plants, Cr(VI) is readily reduced to Cr(III) (Lytle et al., 1998; Aldrich et al., 2003).

This research project was designed to assess the effects of organic matter and plants on the mobility of chromium in soil. In a soil column experiment, we evaluated the oxidation state of chromium throughout the soil depth after a 90-day leaching period. Analyses included evaluation of chromium in soil and leachate, and also plant root and shoot uptake of chromium.

## 2. Material and methods

### 2.1. Soils and treatments

The Ashland soil used in this study was a silt loam obtained from the Kansas State University Department of Agronomy North Agricultural Farm in Manhattan, KS. The soil was analyzed prior to the experiment at the Kansas State University Department of Agronomy soil testing lab. Results of the soil analyses are given in Table 1. Before the study, the soil was ground and sieved to ensure soil uniformity.

Two soil treatments were used in the experiment: untreated Ashland soil and Ashland soil amended with 10% (by volume) composted cow manure. The Ashland soil with compost was mixed thoroughly in a high-capacity mixer to ensure uniformity. Prior to packing the soils into the columns (see below), all soils were amended with potassium chromate, $K_2CrO_4$ (Sigma-Aldrich, St. Louis, MO). The potassium chromate was dissolved in deionized, distilled water to obtain two concentrations. The first concentration was prepared by dissolving 2.49 g $K_2CrO_4$ in 550 g and mixing it with