CHEMICAL DISTRIBUTION OF Cr(VI) APPLIED IN DILUTE SOLUTIONS TO A SANDY LOAM ARGIUDOLLS

by

KEVIN A. CAPPO

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ABSTRACT

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Groundwaters have become contaminated with Cr(VI) at levels that exceed the drinking water standard (>0.50 mg CrL^{-1}) at more than 48 locations in Michigan as well as other places in the United States. Removal of this Cr is expensive and difficult if attempted by chemical means. Chromium may be precipitated by soils which would offer an inexpensive method of removal of Cr from the water; however, due to the low levels in many groundwaters and the necessity of reducing Cr to levels less than 0.05 mg CrL^{-1} to meet drinking water standards, soil properties must be optimum for this to be a viable means of Cr removal.

In a laboratory incubation study it was shown that the surface soil of a Warsaw sandy loam (typic Argiudolls) would reduce total soluble Cr from 1 mg CrL^{-1} to less than 0.05 mg in 48 hours and would reduce Cr from 5 mg CrL^{-1} to less than 0.05 mg in 10 days. Subsoil required a longer

period of time to reduce Cr levels below the 0.05 mg CrL^{-1} level. The Cr which remained in solution was largely as Cr(VI). Both Cr^{3+} and chromate ($Cr_2O_7^{2-}$, or CrO_4^{2-}) were adsorbed by the soil. but chromate adsorption was favored by the subsoil.

Soils with properties similar to the Warsaw soil can be utilized to remove Cr(VI) from solution if a concentration in solution not to exceed 5 mg CrL^{-1} is used and if the retention time is 10 days to 2 weeks.

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INTRODUCTION

In the past industrial wastes have been discharged into the nearest body of water or poured onto the ground. Dumping waste was easy and inexpensive but it led to deterioration of waterways, contamination of soil and in certain cases, to contamination of groundwater. When groundwater becomes contaminated it is very difficult to chemically treat the contaminated plume. Generally the contamination is of a low concentration and the plume tends to spread and become more dilute with time.

In Michigan there are 48 locations where chromium (Cr) levels in groundwater exceed 0.05 mg $Cr \cdot L^{-1}$, the drinking water standard, and is therefore a serious contaminant. An additional 129 sites are potential problems even though Cr has not reached the groundwater in sufficient quantities to exceed the drinking water standard at the present time. When a contaminated plume enters an aquifer used for drinking water or moves toward such an aquifer, some type of remedial action is needed.

Several possible methods exist for treating groundwater contaminated by Cr(VI), but all involve pumping large quantities of water. One method is to chemically treat the water to reduce and precipitate Cr.

In addition to being an extremely expensive procedure, precipitation of Cr to a level that is less than 0.05 mg CrL^{-1} is difficult without using large quantities of chemicals. Disposal of the chemicals used to precipitate Cr may also present some difficulties. A second method is to build a holding lagoon and pond the water until the Cr(VI) is reduced to Cr(III) and precipitated. A lagoon is not only expensive in both money and land, but many soils (especially sands) are not suited for holding ponded water. Construction of holding lagoons on these soils would require clay liners.

A third method is surface application to soils of the Cr contaminated water as irrigation water. This method is relatively inexpensive. If the soil can be used to rapidly reduce and precipitate Cr(VI), while simultaneously not damaging crops, Cr(VI) can be removed from contaminated groundwater safely and efficiently.

The purpose of this study was to evaluate the ability of a Warsaw sandy loam (typic Argiudolls) (surface and subsurface horizons) to remove Cr(VI) from irrigation water. The specific objectives were to:

1. determine the length of time necessary to reduce and precipitate Cr in the soil;

2. estimate the quantity of Cr that can be removed by a soil; and

3. elucidate the mechanism by which Cr is held in the soil (via cation exchange/adsorption or by precipitation).

LITERATURE REVIEW

Chromium (Cr) was first discovered in 1797 in Siberian red lead ore ($PbCrO_4$) by Nicolas-Louis Vauguelin. The following year it was isolated in metallic form from CrO_3 through charcoal and high temperature treatments. Chromium was also discovered to be the source of color in emeralds and other gemstones. Due to these color effects, it was given the name chromium--from chroma, Greek for color (National Research Council, 1974).

Mining sources were developed soon after discovery of the metal. One of the first processes developed was treating chromite ore $[(Fe,Mg)O(Cr,Al,Fe)_2O_3]$ with limestone ($CaCO_3$) and soda ash (Na_2CO_3) to produce chromates (CrO_4^{2-} and $Cr_2O_7^{2-}$). London was the site of the first Cr chemical facility which was started in 1816. By 1822, Cr dyes were produced. Chromium was first used for tanning in 1858, and by 1879, $FeOCr_2O_3$ was produced for refractory use. Metallurgical use began in 1910, which led to the plating industry by 1926.

As a result of the industrial development Cr became a component of the waste generated. Disposal of the waste chemicals from industry has always been a severe problem and Cr as a metal waste was no exception. Contamination of soils and groundwaters have been recorded in many parts of the world.

The first conclusive evidence that Cr was an essential trace element for man was reported in 1955 (National Research Council, 1974). Chromium is thus a metal that is essential for man in low concentrations but quite toxic if in high concentrations.

Chromium Chemistry

Chromium is a transition metal that can be found in a number of oxidation states (-2, 0, +2, +3, and +6). Of these, two states [Cr(III) and Cr(VI)] other than the ground state metal are most important. Chromium used for industrial purposes is largely in the Cr(VI) state and generally in the strong acid form. In this state it is generally combined with oxygen and exists as an anion, the important anionic forms of which are CrO_4^{2-} and $Cr_2O_7^{2-}$. In these anionic forms, Cr is normally soluble, and in acid solutions, Cr(VI) functions as a strong oxidizer. Chromates are used in the plating industry, the tanning industry, in wood preservation and other similar industries.

The Cr(III) form also combines with oxygen, but the cationic Cr^{3+} will precipitate and form the hydroxide and oxide forms that are very insoluble compounds (Cotton and Wilkinson, 1980). The anionic form is mobile in soils and thus easily becomes a contaminate of groundwater if the Cr waste is transmitted to soils either by spilling or through disposal in land fills.

Chromium in the Environment

Chromium is found in air, soil and water. Increased blood sugar levels and cholesterol levels in animals have been associated with Cr deficiency. But Cr may become toxic at relatively low levels (National Academy of Sciences, 1974). Positive growth responses for some crops to Cr have been reported, but Cr has not been proven to be essential for plant growth (Vicini, 1981).

In the earth's crust (continental) Cr is present at levels of 80 to 200 mg $Cr \cdot kg^{-1}$ with an average of 125 mg $Cr \cdot kg^{-1}$. While Cr is commonly found in concentrations from 1 to 1,000 mg $Cr \cdot kg^{-1}$ in soils (Lindsay, 1979), Michigan soils seldom exceed 100 mg $Cr \cdot kg^{-1}$.

Contamination of soils with Cr has come from many sources. Phosphorus fertilizers range from 30 to 3,000 mg $Cr \cdot kg^{-1}$ with an average of about 300 mg $Cr \cdot kg^{-1}$. Their application has given a widespread, low level of Cr addition to soils. Perhaps the most important source of contamination has been from both industrial and domestic waste material. The main industrial sources have been plating, tanning, printing, insecticide, and chemical industries. Corrosion inhibitors are also used heavily by industry. Home use of Cr consists of polishing and cleaning fluids, and corrosion inhibitors which may be discharged into the sewage system and wood perservers which may contaminate soils. Chromium which enters the sewage systems either from domestic or industrial routes becomes a contaminate of sewage sludges. When Cr waste is discharged into a municipal sewage system, it will normally partition strongly to the sludge phase during the treatment process. Therefore, disposal of sludges that are high in Cr can also place this metal into the soil environment.

Direct spills at or near industrial sites often lead to contamination of soils and waters. Most often these spills are in the form of Cr(VI) which exist as the anion form and moves freely with the water unless the Cr(VI) is reduced and precipitated in the soil.

Chromium is taken up by all plants, although the quantity that is accumulated is small and varies with species. Lower order forms such as mosses and lichens take up 10 times more Cr than higher order plants. Vegetable crops accumulate between 0.01 and 1 mg $Cr \cdot kg^{-1}$ dry tissue. Chromate easily penetrates biological membranes, but Cr^{3+} does not. Once inside the cell Cr(VI) is rapidly reduced to Cr(III). The toxicity of Cr(VI) to living cells is from its strong oxidizing potential.

The various forms of Cr in soils have been previously studied. Bartlett and Kimble (1976a) reported on the reactions of trivalent Cr in soils and in a companion paper discussed the reactions of hexavalent Cr in soils (Bartlett and Kimble, 1976b).

Reactions of Cr(VI) in soils have been subject to some controversy in the literature. Carey et al. (1977) found that soluble Cr rapidly converted to insoluble forms in soils with widely varying pH's. The precipitated forms were various mixed oxides of Cr(III) and Fe(III). But Bartlett and James (1979) reported that many soils would oxidize Cr(III) to Cr(VI). The exact properties of the soil which lead to this oxidation were not defined.

Grove and Ellis (1980) found that both Rubicon sand (Entic Haplorthod, pH 4.7) and Morley clay loam (Typic Hapludalf, pH 6.0) reduced Cr(VI) rapidly, and these soils had a capability of reducing rather large quantities of Cr(VI). When the pH of the Morley clay loam was increased to 7.5, the soil still reduced Cr(VI) but the rate of reduction was greatly diminished. A greater quantity of Cr(VI) was reduced by the acid Rubicon sand in one week than was reduced by the limed Morley, pH 7.5, in 16 weeks.

The two factors that appeared to be most important in reducing Cr(VI) were soil pH and organic matter content. Therefore, a management strategy was suggested by these authors which would use organic matter as an electron source and acidifying agents to obtain rapid and complete reduction of the Cr(VI). Once reduction had been completed, increasing the pH of the soil through liming would precipitate the Cr and maintain it in an insoluble form.

In a study of the effect of liming on Cr(VI) removal, James and Bartlett (1983c) showed that liming reduced the amount of Cr(VI) removed from solution by more than half. Generally, they found that about one-third of the added Cr(VI) was removed in a 22 hour shaking period.

Organic complexed Cr(III) may remain soluble for a longer period of time than non-complexed Cr (James and Bartlett, 1983a,b). This could mean that although organic matter would have the desired effect of aiding reduction of Cr(VI), complexation of the reduced Cr might prevent or slow down precipitation.

METHODS AND MATERIALS

Site Selection

An agricultural field was being used to treat groundwater which was contaminated with Cr at the time that this study was initiated. The location was on the Van Orman farm located in Schoolcraft county (S20 of T4S,R11W). Two areas were currently being irrigated with water that contained no more than 0.1 mg $Cr \cdot L^{-1}$ at a rate of 2 to 4 inches per application which added about one Kg $Cr \cdot ha^{-1} yr^{-1}$. A rest period of two weeks was maintained between applications. Sorghum was being grown at the time soil samples were collected.

The choice of using soils from the Van Orman farm for this study was based on two main reasons. First, both the physical and chemical characteristics of the soil should be optimum for reduction of Cr(VI) (Table 1) since the Warsaw sandy loam (typic Argiudolls) has a relatively high organic matter content and a moderately low pH. And second, the Van Ormans farm also had the advantage of being located near (over) a chromate contaminated groundwater plume originating from a wood treatment plant. The highest concentration at any point in the plume was 7.5 mg $Cr \cdot L^{-1}$ (French, et al., 1984).

Soil samples were taken August 25, 1983, from the two areas being irrigated and from a third area which had not been irrigated with Cr contaminated water.

Table 1. Physical and chemical characteristics of Warsaw sandy loam (typic Argiudolls)

	surface 0 - 15 cm	subsurface 45 - 60 cm
pH (water)	6.3	5.2
pH ($CaCl_2$)	5.7	4.3
organic matter (gKg^{-1})	22	10
sand (gKg^{-1})	497	722
silt (gKg^{-1})	362	143
clay (gKg^{-1})	141	135
Total Cr ($mgKg^{-1}$)	35.2	32.2
DTPA ext. Cr (mgK^{-1})	0.005	0.005

The data in Table 2 shows that the total Cr in the soil is very large relative to the quantity of Cr being applied. DTPA extractable Cr was detectable in the soil which had just been irrigated (west circle) but was at or below the detection limit in the soil which had received irrigation 2 weeks earlier (see Table 3).

Table 2. Total Cr in the soil at the Van Orman farm[1]

Depth	West Irrigated Circle	East Irrigated Circle	Non-irrigated Corn Field
cm	mg Cr·kg^{-1}		
0 - 15	37.5	35.2	43.9
15 - 30	42.2	39.2	42.0
30 - 45	40.2	48.6	58.8
45 - 60	26.8	32.2	44.7
60 - 75	20.3	16.6	39.7

[1] The west circle had received irrigation within the last 24 hours; the east circle had received irrigation 2 weeks earlier. Total Cr applied to the irrigated fields would be less than 1.5 pounds/acre.

Table 3. DTPA extractable Cr from the soil at the Van Orman farm[1]

Depth	West Irrigated Circle	East Irrigated Circle	Non-irrigated Corn Field
cm	mg Cr·kg^{-1}		
0 - 15	0.04	<0.01	n.d.
15 - 30	n.d.	n.d.	n.d.
30 - 45	0.03	<0.01	n.d.
45 - 60	<0.01	<0.01	n.d.
60 - 75	0.04	n.d.	n.d.

[1] The west circle had received irrigation within the last 24 hours; the east circle had received irrigation 2 weeks earlier. Total Cr applied to the irrigated fields would be less than 1.5 pounds/acre.

Soil Collection

Samples were collected from the irrigated corn field using a 2.54 cm stainless steel probe for each of the sampling depths. Twenty or more probes were collected at random within each irrigated circle for each depth of samples. The non-irrigated site was sampled with a 7.6 cm bucket auger for both the surface horizon (0 - 15 cm) and the subsurface horizon (45 - 60 cm) to obtain soil for the laboratory study. After sampling, the soil was air dried, passed through a 2 mm plastic sieve and stored in glass bottles.

Soil Analysis

Soil pH was obtained by both 2:1 deionized-distilled water to soil (10 ml to 5 gm) and 2:1 0.01 M $CaCl_2$ to soil (10 ml to 5 gm). Samples were equilibrated for 15 minutes then stirred for two minutes while obtaining each reading. Three replications of each soil sample were tested using a glass combination mini-electrode.

Particle size analysis was performed using the hydrometer method (Day, 1965). Each value reported is a mean of duplicates.

Extractable Cr was determined using the DTPA extractant as given by Lindsay and Norvell (1978). Total Cr was determined by the acid digest method as given by Reisenauer (1982).

Organic carbon was determined using the alternate procedure involving heat of dilution of the routine colorimetric determination of soil organic matter (Schulte, 1980).

Laboratory Studies

A representative surface horizon (0 - 15cm) and a representative subsurface horizon (45-60 cm) were compared to examine the effects of organic matter, pH, and time on removal of Cr(VI) (chromates) from dilute solution.

Five Cr(VI) stock solutions were prepared and used throughout this study. These solutions consisted of a

1000 mg CrL^{-1} stock solution and standards of 10 mg CrL^{-1}, 5 mg CrL^{-1}, 1 mg CrL^{-1} and 0 mg CrL^{-1} Cr(VI) as $K_2Cr_2O_7$ in 0.01 M $CaCl_2$.

For each experiment, 5 grams of soil from either the surface or subsurface horizon were incubated with 10 ml of each working standard in 50 mL polypropylene screw top centrifuge tubes. For each horizon 3 replicates of each of the 4 working standards were run giving a total of 24 samples per experiment. Incubation periods were 5 minutes, 12 hours, and 1, 2, 4, 7, 10, 14 and 56 days at room temperature.

Upon addition of the stock standards to the soil, the 50 ml centrifuge tubes were shaken vigorously for one hour on a side to side, or wrist action shaker. After shaking, the samples were allowed to settle and incubate for the desired period of time. Incubation times started from the moment shaking began, so the 5 minute incubation period received only 5 minutes of vigorous shaking before analysis.

After incubation, the soil was separated from the supernatant by centrifugation and the Cr(III) and Cr(VI) content of the supernatant determined by the method of Mazzucotelli et al. (1983).

The remaining soil was extracted three times with 20 ml of 0.01 M $CaCl_2$, by mixing for 5 seconds at high speed on a vortex mixer followed by 1 hour on the side to side or wrist action shaker. After one hour the samples were centrifuged for 5 minutes at 3000 rpm and the supernatant saved for total Cr analysis. Samples were weighed after each extraction and decantation to account for carryover between extractions. The use of the $CaCl_2$ wash was designed to:

1. remove exchangeable and soluble Cr^{3+};
2. remove free $Cr_2O_7^{2-}/CrO_4^{2-}$ from solution phase; and
3. replace Cr(VI) on anion exchange sites by mass action of Cl^-.

Calcium chloride was used in preference to chelating extractants such as EDTA or DTPA, since it does not depend on time of exposure and should not complex and dissolve freshly precipitated Cr(III) hydroxide ($Cr(OH)_3$). In addition, this method will not oxidize or reduce Cr(III) and Cr(VI), respectively, as will other extracting methods such as citrate-dithionate oe diphenyl carbazide, and coprecipitation with $Fe(OH)_3$ or $Al(OH)_3$ would not be expected. Also in contrast to more thorough extraction methods, use of $CaCl_2$ should not remove strongly adsorbed chromate ions.

After the three $CaCl_2$ extractions, the residual soil was extracted three times with 20 ml of 0.015 M Na_2MoO_4. The procedure is identical to the $CaCl_2$ extracts except that additional centrifugation time and speed were required due to the dispersion effect of Na^+. Centrifuge speed was increased to the maximum (slightly over 3000 rpm) and centrifuge times were increased to 10, 20, and 30 minutes for the first, second and third Na_2MoO_4 extractions, respectively.

Sodium molybdate was used to displace adsorbed Cr(VI) (as chromate or dichromate) through mass action and anionic exchange. Molybdenum was chosen for its similarity to chromate. Although no simple dimolybdate ion can be readily obtained (Cotton and Wilkinson, 1980) in solution to displace Cr_2O_7 directly, dichromate is in equilibrium with chromate ions which can be directly displaced. The dichromate will be displaced also by mass action of a minus two charged anion if not through direct competition. Sodium, or another monovalent cation, must be the counter cation or the molybdate will precipitate rather than displace chromate. After 3 washes of $CaCl_2$ and 3 washes of Na_2MoO_4, all the remaining Cr was assumed to be in a precipitated form.

To determine precipitated Cr, the sample was digested overnight with 2 N HNO_3 at 80^oC. The sample was weighed both before and after incubation to account for concentration effects. The supernatant was then poured into a new 50 ml tube and incubated with 2.5 ml 30% H_2O_2 overnight at 80^oC to remove organic matter from the sample. The new tube, tube plus supernatant, and incubated weight were all taken for determining concentration factors. After incubation an aliquot of solution was diluted 1:3 to produce a 0.5 M HNO_3 solution. Again weights were recorded at each step. The 0.5 N nitric acid solution was then analyzed for total Cr content. Dilution down to 0.5 M acid was to reduce salt buildup during analysis by atomic absorption spectrometry (AAS).

All analysis were performed on a Varian Techtron atomic absorption unit at 357.9 nm as soon as possible after being extracted. Samples were stored at 4 C until analyzed.

Cr(III)/Cr(VI) Determination

A portion of the initial incubation solution was analyzed for Cr^3/Cr^{6+} speciation via a modified method of Mazzucotelli et al. (1983). Two mL of the Amberlite/MIBK/HCl liquid anion exchange solution (LAES) plus two mL of solution were used rather than one mL of each as recommended in the method. The increased volume served to provide enough solution to analyze for Cr by AAS. The LAES complexes the Cr(VI) thereby concentrating Cr(VI) in this phase leaving the Cr(III) in the acid-water phase. Atomic absorption of Cr in the acid-water phase was used to test for Cr(III). The organic phase could not reliably be used because it plugged the intake system, so Cr(VI) was calculated indirectly by subtraction. Work by Mazzucotelli et al. (1983) showed that over 95% of the

Cr(VI) will be in the LAES, and that less than 5% of the Cr(III) will be in the LAES. Preliminary studies varified this result.

RESULTS AND DISCUSSION

Soluble Phase

Chromium added to the soils as Cr(VI) will partition into soluble and insoluble phases. This partitioning and distribution depends on reduction, adsorption and soil characteristics such as pH and organic matter. The most important fraction from an environmental viewpoint is the soluble phase. The soluble phase is responsible for groundwater pollution, so reducing the amount of Cr in soluble form will reduce the risk to groundwater contamination. Effective cleanup will require that the solution phase be reduced to less than 0.05 mg Cr L^{-1} during the period of time that the contaminated water is retained in the soil.

To obtain an understanding of the working dynamics of Cr speciation and distribution in the soil, three treatment levels (1, 5 and 10 mg Cr L^{-1}) were used. The effects of individual treatments will be compared between surface and subsurface horizons and then differences between treatment levels will be discussed.

The distribution of soluble Cr(III) and Cr(VI) with time after the addition of the 1 $mg{\cdot}L^{-1}$ Cr(VI) [as potassium dichromate] is shown in Table 4. Utilizing 10 ml of solution per 5 g soil gave 2 mg of total Cr added per kg soil. Within the first 5 minutes of exposure to the soil, nearly 50% of the Cr in the surface and about 80% of that in the subsurface has been removed from the solution phase. Thus, a small quantity of soil has effectively removed the Cr from the solution phase. This is an important observation because it is difficult to develop a system that will remove low levels of contaminate ions from solution. As time of exposure increases, Cr continues to be rapidly removed from solution by both soil horizons. Within 2 days the water in contact with each soil was below the established drinking water standard for Cr (0.05 mg L^{-1}). Within a week to 10 days soluble Cr was less than the detection limit in both the subsurface and surface horizon.

In all cases for both horizons the concentration of Cr(III) which would exist as Cr^{3+} ion in solution is very low and particularly low compared to total Cr in solution. First, in most if not all time periods the amount of Cr^{3+} in solution is in the same order as the detection limits (0.005 mg CrL^{-1}). The amount of Cr^{3+} present in the solution in contact with surface soil is generally less than that in contact with subsurface soil. This is especially true when Cr^{3+} is taken as a percent of total soluble Cr. About 6% of total Cr in solution is Cr^{3+} in

TABLE 4. Distribution of soluble Cr(III) and Cr(VI) with time after addition of 1 mg Cr(VI)L^{-1}

Time	Surface		
	Cr(III)	Cr(VI)	Cr(T)
	mgL^{-1}		
5 min	0.06±0.01	0.46±0.01	0.52±0.02
1 h	0.01±0.01	0.32±0.03	0.35±0.02
12 h	n.d.[1]	0.26±0.03	0.26±0.03
24 h	0.01±0.007	0.13±0.01	0.14±0.02
48 h	n.d.	0.04±0.02	0.04±0.02
96 h	n.d.	0.012±0	0.012±0.01
168 h	n.d.	0.017±0	0.017±0
240 h	n.d.	n.d.	n.d.
336 h	n.d.	n.d.	0.007±0
56 days	n.d.	n.d.	n.d.
	Subsurface		
5 min	0.034±0.02	0.19±0.02	0.22±0.006
1 h	n.d.	0.15±0.005	0.15±0.005
12h	n.d.	0.08±0.009	0.08±0.009
24	0.015±0.02	0.08±0.02	0.10±0.01
48 h	0.012±0.01	0.016±0.015	0.028±0.008
96 h	0.008±0.005	0.031±0.01	0.039±0.004
168 h	n.d.	n.d.	n.d.
240 h	n.d.	n.d.	n.d.
336 h	n.d.	n.d.	n.d.
56 days	n.d.	n.d.	n.d.

[1] n.d. is less than the detection limit of 0.005 mgL^{-1}.

the surface horizon, while Cr^{3+} is closer to 20% of the total in the lower horizon.

The addition of 5 mg L^{-1} Cr solution to the soil produces results similar to the 1 mg L^{-1} application in that within the first minutes of exposure 37% of the Cr added to the surface and 64% of the Cr added to the subsurface horizon were removed from solution (Table 5). By the end of half a day 56% of the Cr in the surface and greater than 80% of the Cr in the subsurface was removed from solution. This increased to 77% and 86% by day 2 and 98.5 % and 93.1% by the end of one week. By the end of the second week 99.7% of the Cr was removed by the surface and 96% by the subsurface horizon. But the surface horizon required 10 days of contact with solution containing 5 mg L^{-1} Cr to reduce the soluble level to <0.05 mg L^{-1}, the drinking water standard. More than 14 days were required in the subsurface horizon. Initial removal was much more rapid in the subsurface than the surface horizon likely a result of anion adsorption.

Trivalent Cr plays a minor role in the amount of soluble Cr in both horizons. Less than 2% of the soluble Cr is Cr^{3+} for the first 2 days of solution contact with the surface soil. The percentage increasing only as total soluble Cr becomes less than 1 mg L^{-1}. In the subsurface horizon, Cr^{3+} remains at about 5% of the total soluble Cr throughout the first 2 days until the total soluble Cr

Table 5. Distribution of soluble Cr (III) and Cr (VI) with time after addition of 5 mg Cr(VI)L^{-1}

Time	Surface		
	Cr(III)	Cr(VI)	Cr(T)
	mgL^{-1}		
5 min	0.137±0.06	2.99±0.06	3.13±0.02
1 h	0.046±0.04	2.68±0.05	2.72±0.01
12 h	0.041±0.015	2.17±0.17	2.21±0.16
24 h	0.044±0.02	1.71±0.06	1.75±0.08
48 h	0.023±0.016	1.13±0.08	1.15±0.06
96 h	0.046±0.026	0.30±0.10	0.35±0.10
168 h	0.010±0.01	0.07±0.04	0.07±0.02
240 h	0.015±0	0.016±0.01	0.031±0.01
336 h	n.d.[1]	0.007±0	0.013±0.002
56 days	n.d.	n.d.	n.d.
	Subsurface		
5 min	0.087±0.07	1.71±0.07	1.80±0.03
1 h	0.031±0.03	1.30±0.04	1.33±0.02
12 h	0.062±0	0.95±0.006	1.02±0.006
24 h	0.025±0.02	0.99±0.11	1.01±0.12
48 h	0.012±0	0.68±0.05	0.69±0.05
96 h	0.037±0.005	0.70±0.05	0.74±0.05
168 h	0.049±0.01	0.29±0.03	0.35±0.02
240 h	0.025±0.01	0.26±0.003	0.29±0.02
336 h	0.017±0.006	0.18±0.04	0.194±0.03
56 days	n.d.	n.d.	n.d.

[1] n.d. is less than the detection limit of 0.005 mgL^{-1}.

level becomes less than 0.7 mg L^{-1}. After that time the percent of soluble Cr that is Cr^{3+} increased to about 10 percent. Only during the first 5 minutes in the surface soil and 12 hours in the subsoil was the Cr^{3+} levels greater than 0.05 mg L^{-1}. This occurs when reduction has occurred but precipitation or adsorption has not.

The results of the application of 10 mg L^{-1} Cr (VI) to the two soils are shown in Table 6. Initially both soils rapidly remove Cr(VI) from solution. The subsurface horizon removes 55% in the first 5 minutes, 70% after 12 hours and 80% after 2 days. Rapid removal of Cr was complete after two days, but continued slow removal was evident with additional time. The surface horizon starts slower than the lower horizon but continues to remove Cr(VI) from solution at a rapid rate until it is all removed. Only 32% was removed in the first 5 minutes, 44% by 12 hours, and 65% in two days. By 4 days 80% was removed (same as subsurface) and 93% was removed by 10 days. In both horizons more than 2 weeks were required to reduce soluble Cr below the drinking water standard. The subsurface horizon barely reached this level by the 56th day.

For all three Cr(VI) additions the Cr(III) in solution at 5 minutes was much greater in absolute concentration than during the next two or more days. This suggests that initially Cr(VI) is being reduced to Cr(III)

Table 6. Distribution of soluble Cr(III) and Cr(VI) with time after addition of 10 mg Cr(VI) L^{-1}

Time		Surface	
	Cr(III)	Cr(VI)	Cr(T)
		mgL^{-1}	
5 min	0.21±0.11	6.50±0.11	6.78±0.02
1 h	0.07±0.07	6.15±0.14	6.22±0.09
12 h	0.09±0.02	5.53±0.20	5.62±0.18
24 h	0.09±0.05	4.34±0.12	4.44±0.10
48 h	0.02±0.006	3.45±0.06	3.46±0.06
96 h	0.03±0.01	2.06±0.21	2.09±0.20
168 h	0.15±0.02	1.22±0.09	1.37±0.10
240 h	0.03±0	0.70±0.04	0.73±0.04
336 h	n.d.[1]	n.d.	0.23±0.06
56 days	n.d.	n.d.	n.d.
		Subsurface	
5 mim	0.13±0.12	4.28±0.07	4.41±0.06
1 h	0.05±0.04	3.45±0.11	3.50±0.11
12 h	0.18±0	2.82±0.04	3.00±0.04
24 h	0.044±0.02	2.56±0.19	2.62±0.20
48 h	0.024±0.01	2.02±0.09	2.04±0.10
96 h	0.072±0.03	1.98±0.05	2.05±0.07
168 h	0.42±0.01	1.07±0.09	1.49±0.08
240 h	0.072±0.04	1.12±0.09	1.20±0.03
336 h	0.052±0.04	0.90±0.12	0.95±0.09
56 days	n.d.	n.d.	0.04±0.03

[1] n.d. is less than the detection limit of 0.005 mgL^{-1}.

at a rate which exceeds the rate of adsorption or precipitation of an insoluble hydroxide/oxide. The levels of Cr(III) remain low due to several forces acting on the Cr. First, Cr(III) readily forms $Cr(OH)_3$ or one of its corresponding ion pairs; $Cr(OH)_x$, depending upon pH. Not only is the Cr(III) tri-hydroxide insoluble in water, but it (and its ion pairs) are also the substrate for conversion to Cr_2O_3.

The second force is the cation exchange complex. Since Cr(III) exist as the Cr^{3+} cation, it is strongly attracted to the exchange sites and should readily displace mono- and di-valent cations. Complexing with soil bound organic matter is a third method which could keep the level of soluble Cr(III) low.

The difference in effect between application rate is marked. In the surface horizon 48, 38, and 32% of the Cr is removed from solution within the first 5 minutes for the 1, 5 and 10 mgL^{-1} solutions respectively. At the end of one day 86, 66, and 56% has been removed from solution, respectively. After a week, the amount of soluble Cr removed from solution in the 1, 5 and 10 mgL^{-1} treatments was 98%, 97%, and 86%, respectively.

Although a higher quantity of Cr is removed in the 5 mgL^{-1} than the 1 mgL^{-1}, the actual amount left in solution is important. When 1 mg CrL^{-1} was applied, the level of Cr in solution was below safe drinking water standards in

2 days. But 10 days were required to reduce 5 mg CrL^{-1} to levels below 0.05 mgL^{-1} even though a higher percentage of Cr was removed at 7 days for the 5 mgL^{-1} than for the 1 mgL^{-1} treatment. In the 10 mgL^{-1} treatment even after 2 weeks when 98% of the Cr was no longer soluble, the level of soluble Cr(IV) was still over four times the drinking water standard.

The same basic process occurs in the subsoil. Percentage wise, a larger amount was removed in the higher treatments than the lower ones. Again however, the significant factor is in the ability of the soil to reduce soluble Cr levels to below 0.05 mgL^{-1}. This takes less than 2 days after 1 mg CrL^{-1} was applied, greater than 2 weeks after 5 mg CrL^{-1} was applied and nearly 8 weeks after application of 10 mg CrL^{-1}.

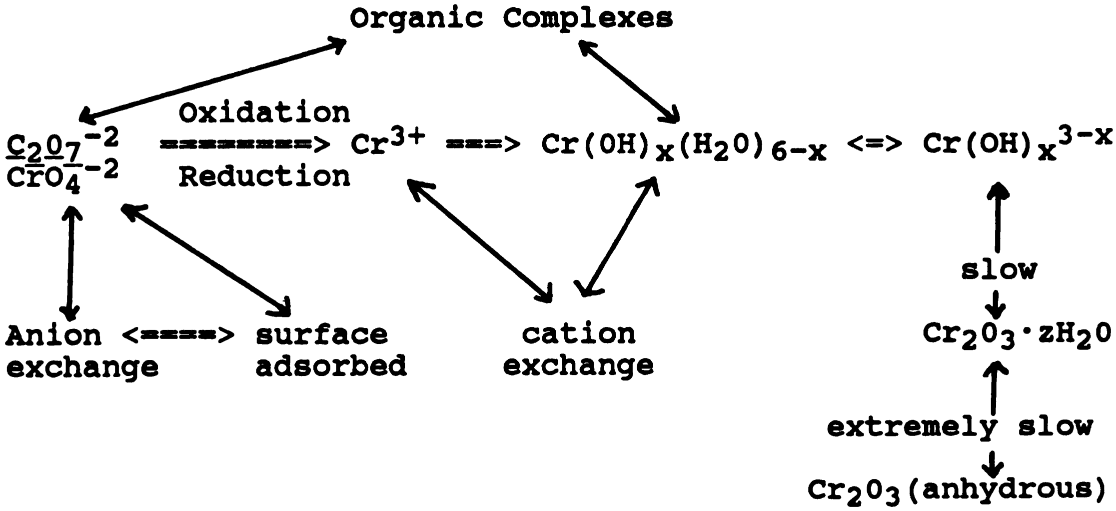
As far as agricultural application is concerned 8 weeks of equilibrtion time is not of real practical value in removing Cr from dilute solutions. Water entering the subsoil would have a required residence time of only 2 days if the solution from the surface was reduced to 1 mgL^{-1} soluble Cr first. Application of water containing 10 mgL^{-1} of Cr could not be used for it takes more than 1 week to reach the 1 mgL^{-1} level. The five mgL^{-1} of Cr is a good alternative since 2 days in contact with the surface soil will reduce the soluble level to 1 mg CrL^{-1} which is required for efficient removal of Cr in the subsurface horizon. Thus reapplication of water could be made safely after a 1 week period of time which is compatible with agricultural operations.

Increased levels of soluble Cr (VI) could be applied if some guarantee existed that the solution would stay longer in the soil. This provides the chance for removal of Cr from the solution phase. This could be accomplished through addition of smaller volumes of water at each application (less percolation). It could also be performed on a deeper profile, providing more soil volume for percolation.

Solid Phase-Exchangeable and Adsorbed Chromium

Once Cr has partitioned to the solid phase, the ability of a soil to hold Cr against dissolution is very important. The longer a soil retains Cr, and the more tenaciously it is held in place, the greater is the chance for precipitation as very insoluble oxides. Once converted to insoluble oxides the Cr should be stable indefinitely as long as soil pH remains in the optimum range for agricultural production.

In addition to retaining the original chromate in the soil, it is also necessary to hold the first product of the reduction process, Cr^{3+}. There are two reasons for this. First, when Cr^{3+} is first formed it must compete with other cations for exchange sites; therefore, it is still mobile and can move with the soil solution until it becomes an exchangeable cation. This is summarized in the following equations.



Secondly any Cr which moves into the subsurface horizon may be more soluble than it was in the surface horizon. The lower pH in the subsurface horizon will shift the equilibrium increasing dissolution of $Cr(OH)_3$, the initial precipitation product of Cr^{3+}. In the surface horizon however, the higher pH favors precipitation of $Cr(OH)_3$, which is likely the first precipitated product formed. In this form the Cr is immobile.

The difference in how Cr is retained in the surface and subsurface horizons is marked (Tables 7 and 8). In the surface horizon the majority of the Cr held was $CaCl_2$ extractable (Cr^{3+}), very little Cr was extracted by Na_2MoO_4 (CrO_2^{2-})· The subsurface horizon by contrast holds nearly as much Cr that is Na_2MoO_4 extractable as was $CaCl_2$ extractable. It is clear from these data that Cr(VI) is reduced much more rapidly in the surface horizon than in the subsurface horizon. This is understandable since organic matter is a principal source of electrons for the reduction process. It is notable that the subsoil is retaining a large fraction of the added Cr(VI) as an exchangeable anion. This fraction appears to be slow to reduce to the Cr(III) form. This may be due to the small source of electrons in the subsoil or to the slow rate at which Cr(III) is precipitated in the subsoil. It required more than 336 hours to remove the Cr from these fractions

Table 7. Distribution of Cr in the solid phase of the surface horizon after addition of Cr(VI)

	Cr(VI) initially added					
	1 mgL^{-1}		5 mgL^{-1}		10 mgL^{-1}	
Time	$CaCl_2$	MoO_4	$CaCl_2$	MoO_4	$CaCl_2$	MoO_4
	Cr adsorbed (mg/kg soil)					
5 min	0.41±0.05	0.04±0.03	2.79±0.04	0.26±0.03	5.80±0.24	0.50±0.001
1 hr	0.54±0.06	0.08±0.07	3.22±0.07	0.29±0.08	6.50±0.08	0.54±0.02
12 hr	0.17±0.08	0.09±0.12	2.09±0.09	0.35±0.08	4.93±0.08	0.63±0.06
24 hr	0.05±0	n.d.[1]	1.22±0.04	0.034±0.02	3.61±0.04	0.14±0.02
48 hr	0.012±0.02	0.04±0.03	1.06±0.08	0.38±0.02	3.49±0.12	0.88±0.05
96 hr	0.012±0.02	n.d.	0.19±0.04	0.10±0	1.71±0.13	0.44±0.02
168 hr	0.023±0.03	n.d.	0.05±0.04	0.08±0.03	1.90±0.11	0.61±0.05
224 hr	n.d.	0.01±0.01	n.d.	0.08±0.06	0.64±0.06	0.35±0.001
336 hr	n.d.	n.d.	n.d.	n.d.	0.20±0.04	0.20±0.08
56 day	n.d.	n.d.	n.d.	n.d.	n.d.	0.08+0.05

[1] n.d. is below the detection limit of 0.01 mgL^{-1}.

Table 8. Distribution of Cr in the solid phase of the subsurface horizon after addition of Cr(VI)

Time	Cr(VI) initially added					
	1 mgL^{-1}		5 mgL^{-1}		10 mgL^{-1}	
	$CaCl_2$	MoO_4	$CaCl_2$	MoO_4	$CaCl_2$	MoO_4
	Cr adsorbed (mg/kg soil)					
5 min	0.40±0.06	0.54±0.02	3.40±0.11	2.09±0.09	7.16±0.09	3.42±0.10
1 hr	0.53±0.04	0.47±0.03	3.65±0.05	2.22±0.06	7.85±0.06	3.67±0.04
12 hr	0.16±0.05	0.47±0.09	3.06±0.02	2.47±0.02	7.12±0.11	4.28±0.16
24 hr	0.24±0.05	0.26±0.07	2.88±0.12	1.83±0.10	6.54±0.13	3.68±0.03
48 hr	0.08±0.02	0.30±0.05	2.18±0.02	2.74±0.08	5.45±0.24	5.59±0.17
96 hr	0.05±0.02	0.19±0.02	1.74±0.08	1.80±0.02	4.64±0.56	3.79±0.10
168 hr	0.02±0.03	0.04±0.05	1.29±0.01	2.10±0.03	4.30±0.20	5.03±0.11
240 hr	0.03±0.02	0.05±0.01	1.02±0.07	1.73±0.02	3.40±0.57	4.54±0.20
336 hr	n.d.[1]	n.d.	0.74±0.12	1.05±0.06	2.87±0.28	3.00±0.15
56 day	n.d.	n.d.	n.d.	n.d.	0.03±0.04	0.46±0.12

[1] n.d. is below the detection limit of 0.01 mgL^{-1}.

in the subsoil. The surface soil, on the other hand, had lost all of the Cr from these fractions by 96 hours except for the highest level of application.

In addition to two different mechanisms involved, it is apparent that for the surface horizon the $CaCl_2$ fraction is the active fraction. Precipitation occurs at the expense of the $CaCl_2$ fraction followed by conversion of exchangeable chromate to the reduced form. For the 1 mg CrL^{-1} application rate, essentially all of the Cr had disappeared from these fractions by the end of 24 hours. For the 5 mg CrL^{-1} application rate, 96 hours were required for removal of most of these fractions. Much longer periods of time were required for precipitation and reduction of the Cr where the 10 mg CrL^{-1} level was applied. This was particularly noticeable in the reduction step. Measurable Cr was replaced by Na_2MoO_4 even after 56 days. This retention of Cr in the fraction extracted by Na_2MoO_4 is even more evident in the subsoil.

Since the subsoil pH would favor reduction as compared to the pH of the surface soil, the reason for failure to reduce the Cr at higher application rates must be attributed to the presence of little easily reducible organic matter in the soils. This suggests a management strategy of supplying fresh or easily decomposable organic matter if larger quantities of Cr are being applied to soils.

The total quantity of Cr removed by precipitation was measured by strong acid digestion of the samples after the repeated displacement extractions and are given in Tables 9 and 10. It is evident that in the surface soil precipitation may readily remove 10 mg $CrKg^{-1}$ soil under the experimental conditions used in this study. This would amount to more than 20 pounds of Cr per acre in the present site that is being used for removal of Cr from the contaminated plume (Van Orman's farm). In addition, the subsoil would also precipitate at least an additional 10 pounds of Cr per acre.

Table 9. Chromium fixed by the surface horizon of a Warsaw sandy loam

	Cr Added (mg/kg soil)		
Time	2	10	20
days	-----Cr fixed (mg/kg soil)--------		
0	0.75	2.10	3.32
2	1.88	6.75	10.2
7	1.95	9.75	15.4
10	1.99	9.87	17.9
14	1.99	9.88	19.2
56	2.00	9.99	20.0

Table 10. Chromium fixed by the subsurface horizon of a Warsaw sandy loam

	Cr Added (mg/kg soil)		
Time	2	10	20
days	-----Cr fixed (mg/kg soil)--------		
0	0.71	1.70	2.43
2	1.57	3.98	5.76
7	1.95	6.07	8.59
10	1.91	6.93	10.1
14	1.99	7.95	12.7
56	2.01	10.0	19.4

SUMMARY AND CONCLUSIONS

Contamination of groundwaters with Cr as chromate is a serious problem in Michigan and other industrial states. More than 48 sites are known in Michigan that contain Cr contamination above the drinking water standard of 0.05 mg CrL^{-1}. Removal of this contamination is a difficult and expensive procedure.

Soils have the ability to reduce and precipitate Cr(VI) under the correct conditions which generally are considered to be high organic matter content and relatively low soil pH's (<6.0). Previous studies have established that Cr(VI) can be reduced when applied to soils in high concentrations. Little was previously known about the rate of removal of Cr(VI) from solution when applied in low levels which are in the range of contaminated groundwater. Little was also known about the fate of the Cr that was removed from solution.

Results from this study substantiate the following conclusions.

1. The surface soil of a Warsaw sandy loam (Typic Argiudolls) removed Cr(VI) to below 0.05 mg CrL^{-1} in 48 hours when applied at a 1 mg CrL^{-1} level. When applied at a 5 mg CrL^{-1} level, it required 10 days to

reach the same level and it required 56 days to reach that level when 10 mg CrL^{-1} was applied.

2. Subsurface samples required much longer to reduce Cr levels below the drinking water standard.
3. Of the Cr that was measured in solution, the large majority was the oxidized form. Removal of Cr(III) by adsorption onto the exchange complex or by precipitation was rapid.
4. A measurable fraction of the adsorbed Cr was removed by extraction with MoO_4 anion and this fraction persisted for a considerable period of time indicating some strong anion adsorption particularly in the subsoil.
5. Fixation of the Cr in precipitated oxides/hydroxides proceeded at the expense of the exchangeable Cr^{3+} fraction.

A final general conclusion is that soils similar to the Warsaw soil can be utilized to remove Cr(VI) from solution if the following general guidelines are followed. The level in the solution which is applied should not exceed 5 mg CrL^{-1}. The retention time in the soil should be 10 days to 2 weeks before making an additional application of water. The level of total Cr applied to the soil should not exceed levels found in natural soils. Once the removal of the Cr has been accomplished, the soil should be limed to a pH of 6.5 or greater and maintained

at that pH. If these guidelines are followed, the method should be inexpensive and satisfactory.

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