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Chromium Cycling in Soils and Water: Links, Gaps, and Methods

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The major links in the cycling of chromium in soils and in natural waters are between chromium(III) and chromium(VI). Between the larger links are lesser links involving processes of mobilization and oxidation of Cr^{III} and reduction of Cr^{VI}. The gaps are mainly in our understanding of the factors that control these processes. If soluble Cr^{III} is added to an "average" soil, a portion of it will become immediately oxidized by manganese oxides to Cr^{VI}. The rest of the Cr^{III} may remain reduced for long periods of time, even in the presence of electron-accepting manganese oxides. However, this less available Cr^{III} can be mobilized by low molecular weight organic complexers and then oxidized where redox conditions are optimal. Usually part of any Cr^{VI} added to a soil or sediment will be reduced instantly, especially under acid conditions. On the other hand, high concentrations of polluting Cr^{VI} may quickly exhaust the readily available reducing power of the matrix material and excess Cr^{VI}, the thermodynamically stable form in air, may persist for years in soils or lagoons without reduction. Cleanup of chromium pollution must involve the surrounding of both Cr^{III} and Cr^{VI} with excesses of slowly available reducing substances and sealing them permanently from inputs of atmospheric oxygen. Monitoring the effectiveness of the measures is mandatory, but fortunately the chemical testing for Cr^{VI} in soil and water is simple and problem free compared with most colorimetric determinations.

The Chromium Cycle

Like the knights seated as equals at the Round Table, scientists find circles satisfying to their souls; and in their quests, they frequently are found traveling around in circles. What goes around comes around. The equality within the chromium cycle (Fig. 1) is an illusion, not unlike that of the Round Table, with King Arthur and his underlings. King Cr^{VI} is the most oxidized, mobile, reactive, and toxic chromium form, and it would be the only existing form if all chromium were to be in thermodynamic equilibrium with the atmosphere. It is fortunate for life on our planet that very little of the earth's soil and water chromium is ever in equilibrium with the air. All of the atmospheric O_2 would be used up before all of the Cr^{III} in the earth's crust could become oxidized to Cr^{VI}. But long before that all life would be poisoned by the chromate formed. Thus, soil chromium is not in equilibrium with the air, nor is soil organic matter. When we find large concentrations of Cr^{VI} in a soil, it usually is because we, the polluters, put it there. Small concentrations can be the result of oxidation of natural Cr^{III}, but larger concentrations usually are the result either of pollution with Cr^{VI} or the oxidation of polluting Cr^{III}.

The reactivities of Cr^{III} species increase as fairly inert crystalline and amorphous minerals are converted to organic and hydroxy-precipitated and polymeric forms of Cr^{III} and then to various more easily oxidized cationic species and mobile, low molecular weight organic species. Sometimes the chromium cycle is kinetically rather sluggish—a slow cycle. Depending on redox conditions and on solubility of Cr^{III}, chromium can become stagnated in the reduced Cr^{III} form and sometimes even in the oxidized Cr^{VI} form. The redox portion of the cycle boils down to simple transformations back and forth between Cr^{III} and Cr^{VI}.

Soils and sediments in partial equilibrium with atmospheric oxygen contain both oxidized manganese and reduced carbon. The oxidation of Cr^{III} to Cr^{VI} by manganese oxides and the reduction of Cr^{VI} to Cr^{III} by soil carbon compounds are both thermodynamically spontaneous reactions. The marvel of the chromium cycle in soil is that oxidation and reduction can take place at the same time. Some of the Cr^{III} added to a sample of an aerobic soil will oxidize, and some of the Cr^{VI} added to the same soil will be reduced.

Persistence of Hexavalent Chromium in Soils and Water

Leaching

Soluble ionic forms of Cr^{VI} formed in or added to soils

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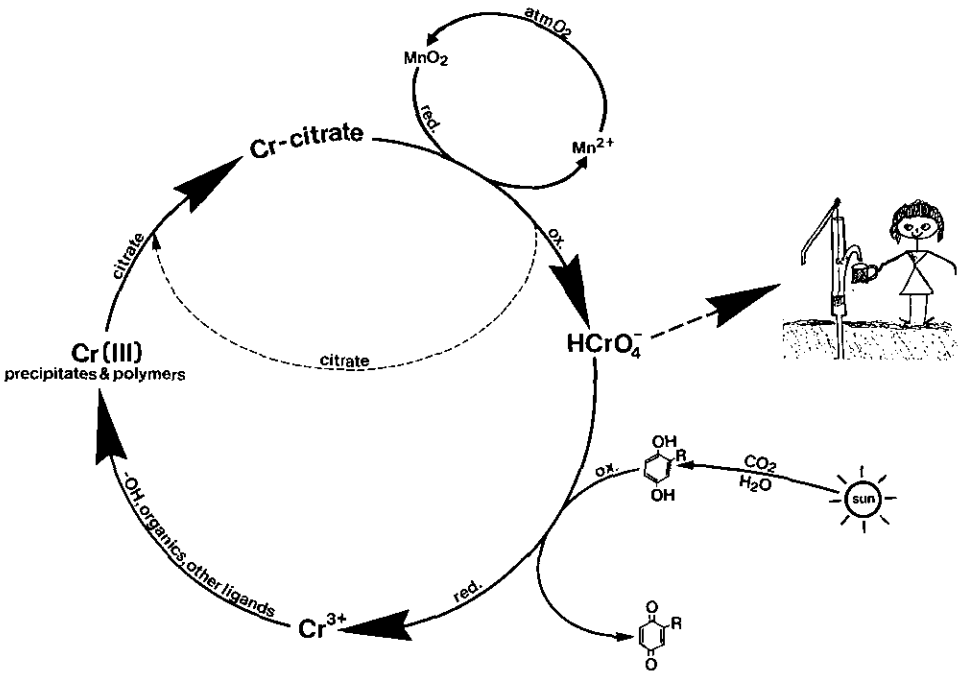

FIGURE 1. Chromium cycling.

or natural waters will persist indefinitely unless chromate is removed by leaching, adsorption, precipitation, uptake by living cells, or by reduction to the trivalent form. Leaching processes have not been studied, but occasional reporting of Cr^{VI} in groundwater is evidence that leaching occurs (*1*). Probably the trace amounts of chromium found in plants enter by root uptake of the hexavalent ion. It seems likely that this form is the most important species of chromium available to plants. High levels of Cr^{VI} are toxic to both higher plants and to microorganisms (*1–3*).

Adsorption and Precipitation

Since both reduction and adsorption can occur simultaneously in many soils, it is not always possible to affix the cause of Cr^{VI} disappearance as being one rather the other. Compared with oxidation kinetics, Amacher and Baker (*4*) found the kinetics of Cr^{VI} reduction to be straightforward and simple, but slower than oxidation. Analogous to adsorption of phosphate anions by ligand exchange, adsorption of $HCrO_4^-$ or $CrO_4^=$ (above pH 6.4) by aluminum and iron oxides and hydroxides and by clay minerals likewise is favored by acidity or other factors that increase the positive charges on soil colloids (*1*). Chromate remaining in the oxidized form in a soil and not extractable by 10 mM $(KH)_{1.5}PO_4$ at pH 7.2 can be considered immobilized, either because it has been precipitated or else bonded tightly by adsorption. Stollenwerk and Grove (*5*) explained adsorption of Cr^{VI} as being driven by positive charges on mineral coatings of iron oxides, and Aoki and Munemori (*6*) showed such adsorption to be accompanied by release of OH groups. James and Bartlett (*7*) found that a significant percentage (sometimes as much as one-half) of Cr^{VI} added to A and B horizons of several northern acid soils dominated by amorphous aluminum and iron oxides and organic complexes was still exchangeable by 10 mM phosphate after gallic acid treatment. This indicated that the Cr^{VI} was protected from reduction by adsorption. More highly weathered southern soils dominated by oxide-rich colloids adsorbed more Cr^{VI} than the less weathered northern acid soil, but these did not bind the Cr^{VI} in such a way as to prevent its reduction.

Reduction of Cr^{VI} in Soils

Added chromate also may be nonextractable from soil material because it no longer exists in the oxidized form; that is, it may have been reduced by electron donors in the soil or water and then adsorbed or precipitated in the Cr^{III} form. The Cr^{III} is likely to be complexed by the organic functional groups that were implicated in its reduction (*1*). As an oxyanion, chromate, like nitrate, is a strong oxidizing agent in acid solutions, meaning that it is easily reduced. However, both nitrate and chromate are much less effective oxidizing agents in neutral solutions or soils, where both have a tendency to persist rather than to be reduced. Even at pH 4, Cr^{VI} is not readily reduced by hydroxylamine, gallic, oxalic, or citric acids, or by hydroquinone. In pH 7.2 phosphate buffer, gallic acid or a water extract of dried soil will reduce Cr^{VI} in the presence of light but not in the dark (*1*). Unlike nitrate, chromate is not reduced by hydrazine. In the process of denitrification, various aerobic and anaerobic heterotrophic soil bacteria that metabo-

lize available organic carbon have the ability to use nitrate as an electron acceptor and thereby reduce it. It seems likely that "dechromification" takes place by similar mechanisms. Amacher and Baker (*4*) showed that reduction of Cr^{VI} by natural organic matter in soil was a first-order reaction with a half-life of several weeks. Chromate reduction by soil and water humic substances consumes hydrogen and consequently is favored by acid additions. In natural soils, the reduction may be extremely slow, requiring years (*8*).

Soil humic acids and fulvic acids in stable, moist field soils do not readily reduce Cr^{VI}. However, drying a soil causes a tearing apart of organic polymers into fragments and exposes and activates and in general converts soil organic matter into easily oxidized material. In other words, after drying, a soil may readily reduce Cr^{VI} when it is remoistened. Soil microorganisms may release easily oxidized (reducing) compounds. Air drying or oven drying of soil samples fosters partial equilibrium between natural soil organic matter and any Cr^{VI} present (*9*). A portion of the soil organic matter is oxidized, and all of the Cr^{VI} is reduced (*10*). Using the EPA acid acetate solution for extracting Cr^{VI} causes a similar reduction of any Cr^{VI} in a soil sample and can be expected to guarantee negative results for chromate presence.

Drying a soil, acidifying it, or freezing and thawing all increase the electron reactivity of the soil organic matter and cause it to be more readily oxidizable by electron acceptors such as O_2 or Cr^{VI} (*11*). Of course, addition of organic substances with a more readily available electron supply, such as fresh, unhumified plant or animal residues or root or microbial exudates, may immediately convert soil or water organic carbon from its metastable equilibrium with atmospheric oxygen into forms that will reduce any Cr^{VI} present, especially when the pH is below 6. Lowering the exposure to the air by filling soil pores with water also can cause an increase in the reducing potency of the soil organic matter.

Using dried and stored samples, earlier workers were not able to demonstrate oxidation in soils of Cr^{III} (*12,13*). They assumed that the thermodynamics between Cr^{III} and soil organic matter prevented the oxidation and that any Cr^{VI} added to a soil would be quickly reduced to Cr^{III}. However, the existence of stable organic matter in soils and sediments in the presence of oxygen testifies emphatically to the nonequilibrium prevailing in them. The kinetic barriers to reduction of oxygen, nitrate, or manganese oxides by soil or sediment organic matter serve to protect Cr^{VI} under many circumstances as well (*10*).

For example, we discovered in the recesses of our laboratory several 1.5-L plastic pots containing soil flooded more than 10 years ago with a 200 mM solution of Cr^{III} (R. J. Bartlett, unpublished data). The supernatant solution had been in contact with the air, even though the pots were covered sufficiently to largely prevent evaporation. About one-tenth of the Cr^{III} had oxidized quickly following flooding a decade ago, and most of the Cr^{VI} remained in solution throughout the 10-year period and is there to this day, in metastable equilibrium with the soil organic matter, which, of course, has the thermodynamic capability of being entirely oxidized to CO_2 by either O_2 or Cr^{VI}. Chromate will persist indefinitely in oxygenated water in metastable equilibrium with an aerobic sediment interfacial surface. However, stirring the sediment is likely to cause the exposure of less oxidized sediment to the supernatant water, and this may bring about reduction of the Cr^{VI}.

The redox interface model of the geometry and chemistry of a pond or waste lagoon presents a very thin boundary between an anaerobic soil or sediment and the water containing dissolved oxygen above it. At this boundary, or interface, there is a tight separation of manganese and iron oxide electron acceptors from the gigantic pool of organic electron donors (*1,11*). Because this thin region of electron acceptor is met with very small portions of reduced substances diffusing during any given time period across the interface, the manganese and iron oxides are reoxidized as fast as they are reduced, and the redox interface endures. Oxidized chromium may persist indefinitely in the aerated water above an undisturbed interface, However, mixing across such an interface will quickly eliminate the oxidized phase and cause reduction of any Cr^{VI} in the water above it and prevent its reoxidation by manganese oxide until the redox interface has reformed.

Oxidation of Chromium in Soils, Sediments, and Water

Mechanisms

In 1979, Bartlett and James (*14*) first reported the oxidation of Cr^{III} added to soils. Earlier work in detecting oxidation in soils had been convincingly negative, regardless of level of Cr^{III} added, original pH, lime, or phosphorus treatments, or aeration, moisture, time, and temperature conditions imposed (*13*). Earlier work was erroneous because dried, stored, so-called soil samples had been studied instead of fresh, moist field samples. Drying alters organic and mineral redox and acidity characteristics so that behavior of the dried sample will change markedly with time during dry storage and while it is returning to its metastable moist state when water is added back (*1,9,11*). Generally, stored dry soils (designated "lab dirt" for emphasis) will not oxidize Cr^{III}.

Bartlett and James (*14*) showed that manganese oxides, present in reactive forms almost universally in fresh, moist, nonacid field soil samples, served as the electron link between the added Cr^{III} and oxygen of the atmosphere and that the amount of Cr^{III} oxidized to Cr^{VI} was proportional to the manganese reduced. These findings were verified by Amacher and Baker (*4*), who studied the kinetics of both oxidation and reduction of chromium. The oxidation of Cr^{III} by soil manganese oxides is controlled by the surface characteristics of the oxides and by the availability of the Cr^{III} to the surface.

Buildup of Mn^{II}, attracted by the negative charge on the oxide surface, leads to slowing of the oxidation of Cr^{III} because the adsorption of reduced Mn^{II} has resulted in a plus-charged oxide surface that repels ionic Cr^{III}.

Factors Affecting Chromium Oxidation

The barriers to Cr^{III} oxidation in soils and waters are kinetic ones. Most of the Cr^{III} species in chromium-polluted soils and waters are insoluble and immobile. Exchangeable trivalent Cr^{III} is practically nonexistent unless the soil pH is below 5. Cr^{III}, a strong Lewis acid, forms a multitude of stable inorganic and organic complexes. Like its soil analog, aluminum, Cr^{III} forms the trivalent hexaqua ion and hexacoordinate complexes with oxygen and soluble polynucleate complexes by hydroxyl group bridging (olation). Past research dealing with behavior of soil aluminum can be helpful in predicting solubility and mobility of Cr^{III} in mineral and organic waste. For example, Cr^{III} appears to be both mobilized and retained in Spodosols in the podzolization process similarly to aluminum (*15*). Chromium tends to be more strongly bound in complexes than is aluminum, and hence chromium has replaced aluminum for tanning leather. Chromium is very tightly bound and immobilized by soil humic acid polymers. The "chrome tanning" of soil organic matter vastly limits the tendency for Cr^{III} to become oxidized and for the organic matter to be decomposed (*2*).

Rate of oxidation of Cr^{III} is determined by the chromium speciation and mobility and by the age of the immobile manganese-oxide surface and its relative freedom from adsorbed, reduced organics and Mn^{II}. The trivalent hexaqua ion will oxidize faster than the trivalent exchangeable Cr^{III}, which will oxidize faster than an olated polymer. Although chromium hydroxides, phosphates, and silicates all are quite insoluble under field conditions, unless the pH is extremely low, freshly precipitated Cr^{III} will oxidize faster than aged materials or well-ordered minerals.

While oxidation of Cr^{III} chelated by low molecular weight organic compounds is slower than that freshly precipitated, it is the Cr^{III} held by these organics that is the most likely to be oxidized in a real-life field soil because it is the only form of Cr^{III} that is mobile enough to find its way to the immobile manganese oxide surface (*16*). James and Bartlett (*3*) concluded that increased chromium uptake by bean plants was a Cr^{VI} effect that resulted from enhancement of $Cr(OH)_3$ solubility by citrate in the soil, which in turn lead to increased oxidation of Cr^{III} by soil manganese-oxides. This is the basis of test method XIII. It is baffling that organic acids appear to act as double edged redox swords, both enhancing oxidation and reduction of both manganese and chromium. By complexing Mn^{III}, organic acids can help drive the reverse dismutation reaction between Mn^{II} and Mn^{IV}. In this reaction, two molecules of organically complexed Mn^{III} are formed, one of which started as a Mn^{II} and gave up an electron to a Mn^{IV}, which on receiving that electron, became a Mn^{III} twin to the electron donating manganese atom. Even though it contains oxidized manganese, Mn^{III}-organic acid complex, formed by reverse dismutation, acts as a reducing agent for Cr^{VI} (*1,17*). We are presented with a paradox where a soil with a high level of manganese oxides is a good Cr^{III} oxidizing soil according to the standard oxidizing test, X, while at the same time the organic acids cause the same soil to be an effective Cr^{VI}-reducing soil because of their reaction with manganese oxides. Strong Cr^{III} oxidizing soils are strong Cr^{VI} reducing soils, and vice versa.

Fortunately, if Cr^{III} is not in a form that is mobile or can be mobilized, it will not be oxidized, in spite of optimum manganese oxide surfaces (*18*). A 5-year experiment with six flooded 10-L plastic "lab lagoons" demonstrated the preservation of tannery sludge Cr^{III} in its reduced form (R. J. Bartlett, unpublished data). Tannery sludge, 1% chromium, was mixed with or sandwiched in between layers of high-manganese soil, 1/1 soil/sludge by volume. The water level was maintained about 5 cm above the soil surface. As evidenced by odoriferous emanations, the lagoons soon became anaerobic. After about 3 months, the odors improved, and the interfacial surface of the soil in contact with the water above became aerobic as indicated by positive tetramethylbenzidine tests (*1*) for manganese oxides. There were occasional short-lived, barely detectable levels of Cr^{VI} in the water, meaning about 0.5 μM. After about a week, there were no more positive tests for Cr^{VI} during the ensuing 5 years of continuous flooding.

The manganese remained oxidized at the surface during the 5 years, and the deeper soil continued to be anaerobic, although the odors did not surface through the interface. After 5 years, sufficient Cr^{VI} was added to each of three lagoons to reach a concentration of 1 mM, and Cr^{III} was added to three lagoons, also at 1 mM concentration. The measured Cr^{VI} in the lagoons receiving chromate declined gradually, until it was no longer detectable after 3 months. In the lagoons receiving Cr^{III}, Cr^{VI} formed overnight and ranged from 20 to 100 μM. It also gradually became reduced until Cr^{VI} was no longer detectable after about 2 months. It is apparent that the high concentrations of sludge Cr^{III} were not oxidized but that added Cr^{3+} was readily oxidized by the manganese oxides that formed at the interface. The Cr^{VI} then diffused downward through the interface into the less well-aerated soil and sludge below and became reduced.

Chemical Methods for Characterizing Environmental Chromium

It is important to note that most chemical methods for measuring redox-related parameters in soils or sediments require that the soils be field moist. Samples should be sieved (4 mm), mixed individually, and stored in double polyethylene bags at 4°C. Results can be ex-

pressed on a dry weight basis by determining moisture on separate samples or on a volume basis (a packed and leveled teaspoon = 5 cm^3).

I. Determination of Cr^{VI} in Water, Soil, or Sediment

a) Extract soil at 3/1 solution/soil ratio, based on dry weight of soil or on a packed spoon volume, with 10 mM K_2HPO_4/KH_2PO_4, pH 7.2.

b) Determine Cr^{VI} by adding 1 mL azide reagent to 8 mL of extract or water, mix, and let stand 20 min and compare color with that in standards (0.5–50 μm) at 540 nm (*1*). Prepare the azide reagent by adding 120 mL of 85% phosphoric acid, diluted with 280 mL distilled water, to 0.4 g of *s*-diphenylcarbazide dissolved in 100 mL of 95% ethanol.

c) Because the Cr^{VI} complex with *s*-diphenyl-carbazide forms so rapidly, there is not time for reduction of Cr^{VI} (*4*), and organic matter does not interfere with color. If cloudiness from precipitated organic or mineral matter is present, it is easily removed following color development using a syringe and 0.2 μm filter while the colored complex remains in solution. Filtration of both standards and unknowns improves sensitivity when Cr^{VI} is below 5 μm.

II. Total Cr^{VI} Reducing Capacity by Soil

This is the classic Walkley-Black (*19*) "total" soil organic matter method. It measures the portion that is oxidizable by Cr^{VI} in the presence of concentrated sulfuric acid, using the heat of dilution. The Cr^{VI} not reduced is titrated with ferrous iron.

III. Available Cr Reducing Capacity

Shake intermittently 2.5 cm^3 of moist soil 18 hr with 25 mL of 0.1 to 10 mM chromium as $K_2Cr_2O_7$ in 10 mM H_3PO_4, filter or centrifuge, and determine Cr^{VI} not reduced in the extract by the *s*-diphenylcarbazide method (see method I). Try 0.1 mM chromium first. If all of the Cr^{VI} disappears, repeat with increased concentrations until the Cr^{VI} remaining is measurable but below 0.1 mM.

IV. Cr^{VI} Reducing Intensity Test

Shake intermittently 2.5 cm^3 of moist soil 18 hr with 20 mL of pH 4.0 NH_4OAc (ammonium acetate), 0.6 M with respect to ammonium, containing 0.5 mM $K_2Cr_2O_7$. Filter or centrifuge and determine concentration of Cr^{VI} remaining (see method I). One mole of chromium is equivalent to 6 moles of manganese plus charge.

V. Potential of Soil to Reduce Contaminating Cr^{VI}

This procedure is identical to method IV, except that soil contaminating Cr^{VI} replaces the added Cr^{VI}.

VI. Potential of Added Organics to Reduce Soil Cr^{VI}

Amend Cr^{VI}-contaminated soil with reducing organic to be tested, shake soil sample with pH 4 acetate buffer, and determine Cr^{VI} remaining, as in procedures IV and V.

VII. Total Oxidizable Soil Cr^{III}

a) Add 40 mL of undiluted laundry bleach solution (5.25% or about 0.7 M NaOCl), adjusted to pH 9.5, to 1.0 g dry soil in a 100-mL glass test tube, and mix using a vortex mixer.

b) Place tube in a boiling water bath for 20 min (hood and goggles), mix again, and obtain a clear extract by centrifuging a portion of the suspension. Determine total chromium oxidized by atomic absorption (AA) or inductively coupled plasma (ICP).

For practical purposes, this test (*4*) measures the total chromium in a soil sample. Hypochlorite readily oxidizes and extracts kinetically inert forms of Cr^{III} such as those in chrome-tanned leather, Cr^{III} previously added to soils as sewage sludge or tannery waste, sewage lagoon sediments, chromite-containing soils, ores, slags, and other chromium mineral wastes. Relative quantities of Cr^{III} oxidized by the citrate/MnO_2 equilibration test (XIII) were well predicted by this determination (*1,8*).

VIII. Available Soil Cr^{III}

Shake intermittently 1 g or 1 cm^3 moist soil with 50 mL of 10 mM K_2H-citrate for 18 hr and determine by AA or ICP the chromium in the extract obtained by filtration or centrifugation.

This test estimates quantities of Cr^{III} that can potentially be leached from soils by soluble, low molecular weight, organic chelating substances. Depending on the level of reactive reducing organics and the oxygen and manganese supply, the Cr^{III} in such soluble organic forms may or may not be readily oxidizable in the field soil. Nevertheless, in a study of oxidizable inert Cr^{III} in leather and sewage sludge treated soils, this test predicted ($r^2 = 0.78$) the quantity of Cr^{VI} formed during long-term MnO_2/citrate equilibration (method XIII) (*8,20*).

IX. Soil Manganese Electron Demand

Shake intermittently for 18 hr, 2 cm^3 moist soil with 12 mL, pH 4.0, NH_4OAc, 0.6 M with respect to ammonium, and 4 mL of 0.2 M KI. Add 4 drops of starch solution (0.3 g potato starch boiled with 50 mL water), and titrate to a colorless end point with 2 mM $Na_2S_2O_3$. Millimoles of thiosulfate per unit of soil are equivalent to millimoles of electrons or plus charge of manganese.

X. Standard Chromium Oxidation Test

Shake 2.5 g of soil (dry weight basis or 2.5 cm^3 packed volume) for 15 min with 25 mL of 1 mM $CrCl_3$ and filter

or centrifuge. If the soil is an adsorber of chromate (high in sesquioxides), shake 15 sec longer after adding 0.25 mL of 1 M pH 7.2 phosphate (method I), and determine Cr^{VI} in the extract according to method I.

A portion of the chromium oxidized during the course of this test is not measured because, depending on the availability of easily oxidizable organic matter, some of the Cr^{VI} formed is reduced during the 15-min period. With dried soils, the reduction frequently equals the oxidation and no Cr^{VI} is measured, even though some chromium was oxidized during the test by remaining manganese oxides not reduced by the drying. Thus, net chromium oxidation is measured.

XI. Preparing Synthetic Amorphous Mn^{IV}

Dissolve 40 mmole of $KMnO_4$ in about 40 mL of distilled water heated to approximately 60°C and transfer with mixing into 30 mL of 2 M $MnSO_4$. Add 80 mmole KOH dissolved in 10 to 20 mL of water. Mix and adjust the pH to 7.5 with KOH or sulfuric acid and let stand overnight with occasional stirring, and then adjust the pH to 6.0 with additional sulfuric acid. There should be no permanganate color remaining. Transfer into dialysis tubing and dialyze against fresh distilled water until the outside solution is close to salt free, as checked by barium precipitation or conductivity. Dilute the suspension to 500 mL or any desired volume. The procedure may be carried out quantitatively so that there are exactly 100 mmole of MnO_2, or a diluted suspension can be standardized by iodine titration as in method IX.

XII. Soil Cr^{III} Oxidizable by Excess MnO_2

Equilibrate a sample of Cr^{III}-contaminated soil in suspension with an excess (0.5–1 mmole per 10 g soil) of synthetic amorphous MnO_2 (method XI). Reduce any remaining Mn^{IV} with NH_2OH without using too much excess and determine Cr^{VI} formed using diphenylcarbazide according to method I.

XIII. Oxidizability of Inert Cr^{III}

a) Weigh 5 g (dry weight basis) of moist or dry soil to be tested into a 125- or 250-mL conical flask, and add 5 cm^3 of moist freshly sampled garden soil that has a pH of 6.2 or greater.
b) Add 0.2 mmole $MnSO_4$, 0.5 mmole K_2H-citrate (made from KOH and citric acid), and enough water to bring the total solution volume to 50 mL.
c) Stopper the flask loosely with a foam plug and place on a rotating shaker providing vigorous horizontal swirling motion.
d) After 3 weeks of swirling, filter or centrifuge some of the suspension, and determine Cr^{VI} in the clear filtrate by the *s*-diphenylcarbazide method (see method I).

This test measures oxidizability of inert soil chromium under optimum conditions of aeration, freshness of manganese oxide surfaces, and a high solubility chelating agent. Mobilizing the inert forms of soil Cr^{III} by chelation with low molecular weight organic acids appears to be an essential first step toward oxidation for this soil chromium. The Cr^{III} oxidized during the 3-week incubation with this test for soils treated with leather waste and sewage sludge was fairly well predicted by the results of a simple extraction of Cr^{III} by pH 5 potassium citrate (method VIII) ($r^2 = 0.78$) (*8*).

Dealing with Chromium Pollution of Soil and Water

Biodegradability

Nonbiodegradable is a bad word in environmental circles. And of course, we know chromium is not biodegradable. No one has given much thought to the millions of tons of leather protein Cr^{III} cross-linked each year to become almost but not quite nonbiodegradable through the chrome tanning process. Soil organic matter can be chrome tanned as well when it is contaminated by chromium waste. Fortunately or unfortunately (there are two ways of looking at it), both leather and soil organic matter can be detanned. In essence, method XIII describes a method for detanning and quantifying chromium bound in inert forms of soil or leather. From the toxic metal pollution standpoint, it is fortunate that detanning is difficult, even though it means we may eventually be up to our ears in old shoes, belts, purses, and motorcycle jackets.

Basement Wall Effect

The formation of colored crusts of chromate on the interior surfaces of basement walls is a spectacular demonstration of toxic and carcinogenic metal pollution and has been reported by the press as such. It is easy to speculate concerning the likely mechanisms for this phenomenon. The most direct mechanism is the chromium analog to the buildup of nitrate on surfaces inside caves, brought about by the evaporative concentration of dilute solutions enriched with nitrate from nitrification of bat guano and moving to the surfaces by capillarity or saturated flow. For this mechanism to quickly concentrate the high levels of chromate that it apparently does would require a fairly high rate of evaporation inside the basement and a high concentration of Cr^{VI} outside the wall.

A second hypothesis also is derived from a nitrate analog, this one at soil/water interfaces in ponds, rice paddies, or lagoons (*11*). The lagoon interface mechanism also has been demonstrated with chromium (*8*). The lagoon interface model starts with Cr^{III} down in the sediment, perhaps recently reduced and hence mobile and reactive. The oxidation of manganese and then chromium occurs in the thin layer of aerobic soil at the sediment surface and in contact above with aerated water, which is in contact with the atmosphere, and below with anaerobic soil. Soluble reduced substances, e.g.,

Mn^{II} and organically complexed Cr^{III}, diffuse into the zone aerated by contact with the atmospheric electron sink, where they lose electrons to become oxidized. Oxidized manganese tends to persist in the aerobic zone; whereas the Cr^{VI}, oxidized by the manganese oxides, is ephemeral. It will gradually diffuse back into the anaerobic zone where it is readily reduced. In the hypothesized wall model, the basement interior is the atmosphere, the porous wall itself is the analog of the aerated water of the lagoon model, and the thin layer of aerated soil next to the outside wall surface is the analog, standing on its edge, of the aerated soil surface between the atmosphere and anaerobic soil, parallel and also vertical and farther away from the aerated wall. Manganese oxides could be expected to accumulate in the thin layer of aerobic soil on the outside surface of the wall where it will oxidize soluble Cr^{III} as it moves by capillarity or even saturated flow from the bulk outside soil toward the high tension moisture gradient, created at the wall by evaporation of water from the inside of the wall. Oxygen diffuses from the basement atmosphere through the wall and to the outside surface of the wall where it oxidizes manganese (*21*) and, thereby, indirectly, chromium.

A major difference in the wall model compared to the lagoon model is that the Cr^{VI} will not diffuse into the anaerobic zone and be reduced in the manner of nitrate of Cr^{VI} in the lagoon. It will tend to remain oxidized, and the concentration of Cr^{VI} on the inside of the wall will continue to increase by evaporation for as long as the outside supply of reactive Cr^{III} lasts. Because of evaporation, the inside basement wall should be a much more effective accumulator of chromate than a pond or paddy soil surface. Testing this hypothesis should be a matter of applying analytical methods I, VII, VIII, and X, and possibly also III, IV, and V, to a horizontal continuum of soil samples beginning at the outside surface of the wall. A physical mini-model would be helpful as well for empirically testing the hypothesis.

The Chromium Stakes

We have a societal stake in naturally occurring chromium minerals (chrome ore) that serve as industrial chromium sources for steel alloys, plating, and leather, and we also have a public interest in pollution by chromium waste of our natural waters and of the earth's unconsolidated surficial material (loosely, soil). Our study of the chemical and biological transformations and fates of chromium in soils, sediments, and waters is, in effect, study only of polluting forms of chromium. We need to fully understand the basic behavior in soils of polluting chromium in order to be able to identify problems associated with biological health and to learn how to manage polluted sectors of our environment in ways that will eliminate the health risks by controlling the conditions causing them. Beyond knowledge, we need an economic commitment to clean up our chromium messes and at the same time abolish chromium waste by recycling the chromium in it. Perhaps we also need to return to the days of oak galls, acorns, and alum for tanning and opt for overall less glitter on our various metal possessions. We are like the chap who quit church because he already knows better than he does. Naturally, we should pursue our quest for learning to understand, but, in the meantime, we are up to our elbows in the waste. We know how to map the polluted areas, analyze for bad Cr^{III}, prevent its mobility, prevent its oxidation to worse Cr^{VI}, analyze for Cr^{VI} in the presence of Cr^{III} and organic matter, reduce the Cr^{VI}, move it, cover it up, stabilize it, and protect ourselves and future generations from its malevolent effects.

General Outline of a Cleanup Approach

Mapping and Sampling

Systematic mapping of soils and unconsolidated mineral and organic materials that may or may not be considered soils in areas suspected of being polluted by chromium is required to determine the extent and the anatomy of the problem. This mapping should be carried out by soil scientists with experience in setting up and using highly detailed mapping units. Then "soils" should be sampled by horizon, employing statistical control to ensure that all mapping units and areas are adequately represented.

Chemical Analysis of Soil Samples

Each of the analytical procedures that we outlined could contribute to overall insight in predicting behavior of contaminating chromium, but the most useful for planning cleanup operations would be determination of Cr^{VI} in a soil (method I), total chromium (method VII), available Cr^{III} (method VIII), standard net Cr^{III} oxidation test (method X), and the test for Cr^{III} that is oxidizable (method XII).

Reduction and Immobilization of Contaminating Chromium

There are only two basic requirements for long-term isolation of chromium waste: a permanent reducing environment and permanent immobilization of reduced chromium. As long as all Cr^{VI} has been reduced and all Cr^{III} is bound by decay-resistant organic polymers, the chromium will remain inert and immobile, provided that oxygen is excluded. In other words, it will not be necessary to seal such a landfill on the bottom to prevent leaching but only to pave the top to prevent oxygen entry. Perhaps composting of chrome slag or contaminated soil with sawdust and sewage sludge or cow manure (in tremendous surplus in land-deficient areas) could provide a final product that would meet the criteria of decay resistance and high molecular weight polymeric material with absence of low molecular weight

"detanning" organic acids. Formulation of any mix would depend, of course, on the earlier analytical results, and the mix would need to be tested experimentally in small batches. A continuously flooded chromium waste lagoon containing a high level of organic matter (manure or sewage sludge) also would serve as a permanent solution to the Cr^{VI} problem, but low molecular weight nonhumic organics possibly could lead to mobilization of Cr^{III} from a leaky lagoon.

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