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Chemistry of Chromium in Lakes

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NWRI Contribution # 93-16

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CHEMISTRY OF CHROMIUM IN LAKES

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ABSTRACT

The inputs of industrial wastes have changed the levels and forms of chromium in many lakes and there is growing concern about the accumulation of Cr(VI), a known carcinogen, in drinking water supplies. This report provides a critical review of the effects of speciation, transformations and solubility on the cycling of chromium in lacustrine environments. Unique features of chromium dynamics associated with the decoupling of redox-driven chromium cycle from those of iron and manganese at the sediment-water and air-water interfaces are highlighted. Reductive precipitation is important in the immobilization of pollutant chromium in sediments. Photooxidative dissolution of Cr(III) especially at the air-water interface is identified as a key area for further research. The available database is inadequate for establishing any linkages between the Cr and biological cycles in lakes.

Key words: chromium, lakes, cycling, speciation, redox, geochemistry

Introduction

The aqueous geochemistry of chromium shows an interesting paradox in terms of the contrasting behavior and toxicities of the two principal redox species (Murray et al., 1983; Campbell and Yeats, 1984). Trivalent chromium is a hard acid with a tendency to form strong, kinetically inert complexes involving a variety of ligands found in the environment. The principal aqueous Cr(III) species are Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_3^0$, and $\text{Cr}(\text{OH})_4^-$, with Cr^{3+} being prevalent at $\text{pH} < 3.6$ (Elderfield, 1970; Rai et al., 1987). The solubility of Cr(III) in soils and natural waters is limited by the formation of highly insoluble oxides, hydroxides and phosphates. Dissolved Cr(III) has a strong tendency to adsorb to surfaces (Cranston and Murray, 1980) and like other first-row transition metals, it has a catholic affinity for O-, N- and S-containing ligands and hence can form a multiplicity of organic complexes in natural waters (Nakayama et al., 1981b). Thus, in nature, Cr(III) behaves very much like Fe(III) and may be classified as a scavenged element and potentially can be used as a tracer for transport and mixing in lakes (Burton and Statham, 1990). Because of the tetrahedral coordination of Cr(VI) compared to hexagonal coordination of Cr(III), the redox potential for the Cr(VI)/Cr(III) couple is so high that few oxidants in natural waters are capable of effecting the reaction. In particular, the oxidation of Cr(III) by dissolved oxygen is kinetically very slow (Eary and Rai, 1987).

The chemistry of Cr(VI) is radically different from that of Cr(III). Hexavalent chromium forms a number of stable oxyacids and anions including $\text{Cr}_2\text{O}_7^{2-}$ (dichromate), HCrO_4^- (hydrochromate), and CrO_4^{2-} (chromate), the last two being the only species of any environmental significance. Because of its large ionic potential and tetrahedral coordination, the chromate ion is both a strong acid and an oxidizing agent.

Hexavalent Cr is not readily adsorbed to surfaces and since most of its salts are soluble, Cr(VI) is very mobile in the environment. In terms of its chemical behaviour, Cr(VI) can be classified as a conservative element and hence should have a relatively long residence time in the water column and transportable in groundwater. The high oxidizing potential, high solubility and ease of permeation of biological membranes combine to make Cr(VI) more toxic than Cr(III). An analogy can be drawn between the environmental chemistries of Cr(VI), sulfur and molybdenum. The thermodynamically stable forms of all three in oxygenated waters are tetracoordinated oxy-anions of identical charge and nearly identical size. All three are actively acquired by plankton using the same anion channels. None of the three oxy-anions strongly sorbs to inorganic surfaces such as clays, ferric oxyhydroxides, alumina or organic matter and none of the elements strongly bioaccumulates. Chromium however differs from the other two elements in that it is very readily converted to Cr(III) by a host of reducing agents commonly found in soils and the aquatic environment such as S^{2-} , Fe(II), fulvic acid, low molecular weight organic compounds and proteins (Rai et al., 1989; Saleh et al., 1989).

The toxicities of the two redox species are equally divergent: Cr(VI) is a known carcinogen and much more toxic in mammalian systems than Cr(III) which is required for glucose, lipid and protein metabolism. As expected, the attention of legislators is now turning increasingly to the actual forms of chromium in key environmental media. Little information is currently available on the speciation of chromium in our freshwater resources and most of the water quality guidelines have been based on total chromium concentrations. In this report, a critical evaluation of the literature on the chemistry of chromium in aquatic environments has been made in an effort to discern the processes that govern the speciation and hence the bioavailability and toxicity of chromium in lakes.

Sources of Chromium in Lakes

Chromium is a vital commodity for which there is no ready substitute. Industrial consumption of chromium (as chromite) has mushroomed from about 100,000 metric tonnes in 1904 to over 10 million tonnes in 1988 (Nriagu, 1988a). On a tonnage basis, chromium ranks 4th among the metals and 13th among all mineral commodities. The global consumption is distributed among three principal end uses: 76% metallurgical, 13% refractory and 11% for chemicals. The end uses in the United States are about 58% metallurgical, 23% chemical and 18% refractory (Nriagu, 1988b). Although each use category generates wastewaters contaminated with chromium, the heaviest pollution loads are associated with the production and use of soluble Cr(VI) compounds. About 20-30% of all the Cr used annually is in the form of Cr(VI). Industrial processes thus tend to generate and disperse the more toxic and mobile Cr(VI) in the environment.

The principal sources of chromium in surface waters include electroplating and metal finishing plants, leather tanning, wood treatment, and fabric dyeing facilities, pigment and cement industries, cleaning (industrial and domestic) solutions, drilling muds and the fallout of chromated aerosols (Nriagu, 1988b; Nriagu and Pacyna, 1988). In developed areas, street runoff and corrosion of steel and chrome-coated structures can become major contributors of chromium to lakes (Ayres et al., 1985). The common use of chromium by many small industries is reflected by the high concentrations in municipal wastewaters. The geometric mean concentrations of chromium in raw sewage entering 37 municipal water pollution control plants in Ontario range from 10 to 560 ug/l with the average being 170 ug/l (MOE, 1991). Similar Cr concentrations have also been reported in wastewaters of Regina, Edmonton, Calgary, Winnipeg and Vancouver (Viraraghavan and Rao, 1991). After treatment, the effluents are generally left with 10-30 ug/l Cr, while the landfill sites for the chromium-rich municipal sludges have become well-known sources for Cr pollution of groundwater and surface waters (Calder, 1988).

Solid waste dumpsites often contain large quantities of steel, chrome-coated and chrome-painted objects and hence represent a potential source of chromium pollution in surface waters.

It has been estimated that about 142,000 tonnes of chromium are discharged annually into the world's aquatic ecosystems (Nriagu and Pacyna, 1988). Assuming that only 10% of the pollutant Cr is discharged first into lakes and rivers, the average concentration in these waters (volume: 1.3×10^{16} liters) would be increased by approximately 1.0 ug/l. Lakes and rivers with elevated Cr concentrations above this value, and which can be attributed to industrial pollution, are found in most parts of the world including the developing countries.

Since chromium-bearing minerals are very resistant to weathering (hence the preponderance of detrital Cr minerals in lacustrine sediments), the concentrations of Cr in unpolluted lakes typically vary from 0.02 to 0.10 ug/l (Borg, 1987; Rossmann and Barres, 1988; Balistrieri et al., 1992). The baseline values may be compared with the average concentrations of total (dissolved + particulate) chromium in the Great Lakes: 0.09 ug/l in Lake Superior, 0.13 ug/l in Lake Huron, 0.39 ug/l in Lake Erie, 0.68 ug/l in Lake Michigan and 0.81 ug/l in Lake Ontario (Rossmann and Barres, 1988). A regional pattern in intensity of Cr pollution is evident in the increase in concentration from the fairly pristine Lake Superior to the more polluted Lakes Ontario and Michigan. The dissolved concentrations average 0.08 ug/l in Lake Superior, 0.07 ug/l in Lake Huron, 0.27 ug/l in Lake Erie, 0.68 ug/l in Lake Michigan and 0.71 ug/l in Lake Ontario, implying that 70-90% of the chromium is in the soluble form (Rossmann and Barres, 1988). Much higher concentrations have been reported in many tributaries and harbours of the Great Lakes where industrial and municipal effluents are typically discharged. For example, the 12 tributary rivers flowing into Lake Superior average 1.4 ug/l Cr (Poldoski et al., 1978); Johnson (1991) likewise found the average chromium concentration in rivers and streams draining into Georgian Bay to be 1.4 ug/l. The concentration in

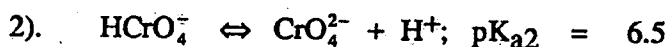
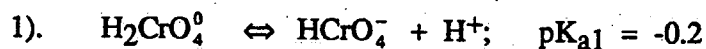
Hamilton Harbour in 1984 was 3.0 ug/l (Harlow and Hodson, 1988).

Average Cr concentrations in lakes and rivers of Ontario vary from 1.2 ug/l in the northern region to 5.5 ug/l in the more developed southeastern area (MOE, 1991). A summary of the reported Cr concentrations in lakes is presented in Table 1. The literature data thus suggest that chromium concentrations in polluted lakes generally fall in the range of 0.5 to 5.0 ug/l. By comparison, the total Cr concentrations in the drinking water of the United States range from 0.4 to 8.0 ug/l and average 1.8 ug/l (*Syracuse Research Corporation*, 1989); the average concentration in Canadian drinking water is also about 2.0 ug/l (Meranger et al., 1979).

Outline of Aqueous Chemistry

Although chromium can exist in nine different oxidation states, from (-II) to (VI), it is found almost exclusively as reduced Cr(III) and oxidized Cr(VI) under most environmental conditions. The speciation of Cr is controlled by the pE and pH of the system. Assuming thermodynamic equilibrium, the stability field of each species can be defined using the available dissociation constants. The plot from Palmer and Wittbrodt (1991) is shown in Figure 1 to illustrate the dominance fields of the more important Cr species under changing pE and pH conditions.

The two dissociation reactions and the associated equilibrium constants for chromic acid are represented by:



Under oxidized conditions Cr(VI) would occur as HCrO_4^- at low pH (<6.5) and as CrO_4^{2-} at higher pH. It is also possible to form the hydrochromate ions, HCr_2O_7^- and $\text{Cr}_2\text{O}_7^{2-}$ at high total Cr(VI) concentration ($> 10^{-2}$ M) and pH values below 4.7 (Baes and Mesmer, 1976), conditions that are unlikely to be observed in lakes (Rai et.al.,

1989).

Under moderately reducing conditions Cr(III) dominates (Figure 1). Possessing one of the higher octahedral site preference energies available to the transition metals (Burns, 1970), Cr(III) forms kinetically inert complexes with various ligands which can persist even under thermodynamically unfavorable conditions. The rates of ligand exchange are often slow, as shown by the second-order rate constant for the exchange of one water molecule in the primary solvation shell of Cr(III) which has been estimated to be $3.6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (Burgess, 1992).

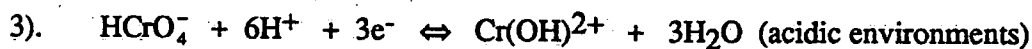
The Cr(III) readily forms octahedrally coordinated cationic or anionic complexes with a large number of ligands, the amphoteric character being dependent on the number and charge of the ligands attached. The most common ligand that reacts with Cr(III) is the hydroxyl anion (Fig.1), the most stable the hydrolysis products being $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$ and CrO_4^- (Rai et.al., 1987). The available thermochemical constants have led to some disagreement as to the dominant hydroxy species; Figure 1 indicates that Cr^{3+} and $\text{Cr}(\text{OH})_2^+$ are not formed to any significant degree within the pH range from 4 to 14. Cr(III) also forms complexes, to a lesser extent, with such ions as SO_4^{2-} , Cl^- and F^- (Richard and Bourg, 1991; Saleh et.al., 1987), may react with CO_3^{2-} and $\text{B}(\text{OH})_4^-$ (Pettine et.al., 1991), but complexing with such ions as PO_3^{3-} , HPO_4^{2-} and H_2PO_4^- has not been investigated (Erel and Morgan, 1991). In acidic solutions (pH < 4.0) with high Cr(III) concentrations, polynuclear complexes are formed through the linkage of adjacent atoms by hydroxo- and oxo-bridges (Stunzi et.al., 1989; Burgess, 1992). These complexes are unlikely to be formed in lacustrine environments, however (Rai et.al., 1987; Pettine and Millero, 1990).

One of the first investigations of natural organo-Cr complexes in surface waters was undertaken by Nakayama and co workers (Nakayama et.al., 1981 a,b,c,d). They found that the most effective complexing agents in pure water were low molecular weight, polybasic organic acids like citric, malic and ascorbic acid; monobasic higher

fatty acids and amino acids had little effect. In contrast to these findings, Mayer et.al. (1984) found that high molecular weight dissolved/colloidal substrates bound more efficiently to Cr(III) than low molecular weight fractions. In fact, the use of Cr(III) in leather tanning, introduced in 1854, depends on its propensity to form stable complexes with proteins, enzymes, cellulosic material, dyestuff and synthetic polymers (Nriagu, 1988a). Apparently, there is no shortage of organic molecules that can react with Cr(III) in lakes. The higher biological productivity, the smaller depths and large sediment-to-water volume ratios imply rapid degradation of organic matter which can result in metal-organic complexation being more prevalent in freshwater environments compared to the ocean.

Controversy in Geochemical Cycle of Chromium

The geochemical cycling of chromium in lakes is determined by a combination of hydrodynamic, chemical and biological processes. The interplay can be illustrated by considering the interconversion of Cr(VI) and Cr(III) over the pH range of 4 to 9 which can be described by the following two reactions:



From the standard electrode potentials and free energies of formation, the following relationships between Cr(III) and Cr(VI) as a function of pH and Eh have been derived:

$$5). \quad \text{Eh} = 1.30 - 0.020 \log\{\text{Cr(OH)}_3^0 / [\text{HCrO}_4^-] \} - 0.118 \text{ pH}$$

$$6). \quad \text{Eh} = 1.17 - 0.020 \log\{\text{Cr(OH)}_3^0 / [\text{CrO}_4^{2-}] \} - 0.098 \text{ pH}$$

According to the equilibrium reactions, equimolar concentrations of Cr(III) and Cr(VI) should be expected in lakes where the pH is 8.0 and the Eh is about 400 mV. This prediction is rarely confirmed by field measurements. For instance, Johnson et al. (1992) and Masscheleyn et al. (1992) could still detect significant concentrations of Cr(VI) in

water samples with low (<200 mV) Eh values. The field data simply show little agreement with the predicted abundance of the redox species in natural waters (Table 2). A number of explanations have been proposed for this discrepancy, including site specific conditions (like point sources, local biota and climate) and the time of year during which sampling occurred (Cranston and Murray, 1980); slow attainment of redox equilibrium due to kinetic restraints (Ekert et.al., 1990); the stabilization of Cr(III) by complex formation with DOC (Nakayama et.al., 1981a); or problems associated with the analysis of trace metals at nanogram levels, such as incomplete separation of the redox species (Johnson, 1990; Pankow et.al., 1977; Osaki et.al., 1983; Cranston and Murray, 1980). All these factors that determine chromium speciation are also related to the following key processes that affect the distribution and ultimate fate of the element in lakes: (i) authigenic precipitation of mineral phases, (ii) scavenging by adsorption onto settling particles, (iii) reduction/oxidation reactions coupled to the cycling of elements such as S, C, Fe and Mn, (iv) bioaccumulation and biotransformation, (v) photolysis and (vi) hydrodynamic forces

The importance of these processes and reaction pathways in the geochemical cycling of chromium in lacustrine environments (Figure 2) are discussed in detail below.

Dissolution/Precipitation of Chromium Minerals

Although over 40 chromium-containing minerals are known and hundreds of insoluble chromium compounds have been synthesized (Nriagu, 1988b), the number expected to form and persist in lacustrine environments is limited. In nature, the most common chrome minerals include chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$), crocoite (PbCrO_4), vauguelinite ($\text{Pb}_2\text{Cu}(\text{CrO}_4)(\text{PO}_4) \cdot \text{OH}$), chromium varieties of magnetite (Loring, 1979) and hematite (Schwertmann et al., 1989), and various chromium containing silicates such as uvarovite ($\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$), krinovite ($\text{NaMg}_2\text{Cr}(\text{Si}_3\text{O}_{10})$) and pyrope. In lakes, these

minerals are likely to occur in detrital form in sediments, and have been shown to account for 76-98% of the chromium in the St. Lawrence River sediments (Loring, 1979). Since most lake sediments tend to be reducing, it is unlikely that the detrital chromium minerals are mobilized by conversion to Cr(VI).

A number of anthropogenerated chromium minerals have been reported. Iranite ($\text{PbCrO}_4 \cdot \text{H}_2\text{O}$), tarapacaite (K_2CrO_4) and crocoit have been identified in plating tank sludges in Corvallis, Oregon (Palmer and Wittbrodt, 1991). Chromatite (CaCrO_4) was likewise isolated in a drainage ditch containing the plating wastes. The ore processing residues in Hudson County, New Jersey contain chromatite, calcium aluminochromate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCrO}_4$), tribasic calciochromate ($\text{Ca}_3(\text{CrO}_4)_2$), and basic ferric chromate ($\text{Fe}(\text{OH})\text{CrO}_4$) (Burke et al., 1991). The formation of hashemite (BaCrO_4) (see figure 4) and related compounds with a generalized composition of $\text{Ba}(\text{Cr}_x\text{S}_{1-x})\text{O}_4$ has been recorded in chromium contaminated soils (Rai et al., 1989) and at the plating dump sites in Corvallis (Palmer and Whittbrodt, 1991). The formation of some of the minerals above and their analogs in lakes can be expected especially near point sources of chromium pollution.

Laboratory studies suggest that the concentrations of chromium in aquatic environments can be limited by the formation of amorphous $\text{Cr}(\text{OH})_3$ or crystalline $\text{Cr}(\text{OH})_3 \cdot \text{H}_2\text{O}$ in the pH range of 6 to 12 and by Cr_2O_3 (eskolaite) under more acid (pH < 6) conditions as indicated in Figure 3 (see also Rai et al., 1989; Richard and Bourg, 1991). In the presence of iron, a number of stable solid solutions can be formed including $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ — the hydroxide series (Figure 3); $\text{Cr}_x\text{Fe}_{1-x}\text{OOH}$ — the goethite-bracewellite series; and $\text{Fe}_x\text{Cr}_{2-x}\text{O}_3$ — the hematite-eskolite series (Sass and Rai, 1987; Schwertmann et al., 1989). These ferrochromium minerals are probably formed in sediments during the reduction of Cr(VI) by Fe(II) and can play a role in the immobilization of chromium in lakes. Recently, Pettine et al. (1991) reported that Mg^{2+} ions in seawater lowered the oxidation kinetics and increased the aging of Cr(III). The

effect was attributed to the formation of mixed Mg-Cr hydroxides with the formula $\text{Cr}_x\text{Mg}_{(1-x)}1.5(\text{OH})_3$, similar to the Fe-Cr hydroxide solid solution discussed above. Such a phase may be formed in lakes with unusual chemical composition.

In contrast to the Cr(III) compounds, the solubility of pure Cr(VI) compounds are so high that their precipitation is unlikely to be an important buffer mechanism for Cr(VI) concentrations in lakes. Figure 4 shows the effects of pH on the solubilities of BaCrO_4 ($\log K_{\text{sp}} = 9.7$) and PbCrO_4 ($\log K_{\text{sp}} = 13.7$), two of the least soluble of the Cr(VI) compounds. Even under the most favorable circumstances, the dissolution of PbCrO_4 in pure water will result in Cr concentration of about 5 ug/L (Figure 4), well above level in most lakes. Chromate, however, can form much less soluble solid solutions with sulfata, phosphate and similar molecules. Rai et al. (1988) proposed that Cr(VI) concentrations in fly ash leachates may be controlled by precipitation/dissolution of phases in the BaSO_4 - BaCrO_4 solid solution.

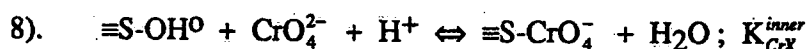
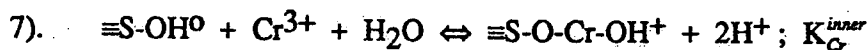
Lacustrine environments also favor the formation of many other low temperature minerals which remain difficult to identify or have not been sought for. In aerobic systems, for example, donathite $(\text{Fe}^{2+}, \text{Mg}, \text{Zn})(\text{Cr}, \text{Fe}^{3+}, \text{Al})_2\text{O}_4$ can readily be formed by the coprecipitation of the constituent metal oxyhydroxides; the coprecipitation of Cr and Al has already been reported in soils by Bartlett and Kimble (1976). In more reducing environments, mixed sulfide minerals such heideite $[(\text{Fe}, \text{Cr})_{1-x}(\text{Ti}, \text{Fe})_x\text{S}_4]$ may be formed when Cr(VI) is reduced. In carbonate rich lakes, the formation of beresovite $(\text{Pb}_6(\text{CrO}_4)_3(\text{CO}_3)\text{O}_2)$ and vauquelinite (see above) should be possible if the lead levels are elevated. Pyromorphite $(\text{Pb}_5(\text{PO}_4)_3\text{OH})$ is an extremely insoluble mineral that occurs widely in the environment (Nriagu, 1984; Cotter-Howells and Thornton, 1991). The replacement of PO_4 by CrO_4 can lead to the formation of embreyite $(\text{Pb}_5(\text{CrO}_4, \text{PO}_4)_3\text{OH})$ in sediments with high Cr(VI) concentrations.

The wide range of redox conditions and metal concentrations favor the formation many chromium minerals even in unpolluted environments. Where they form and how

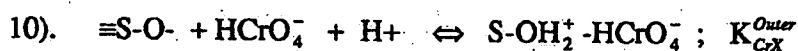
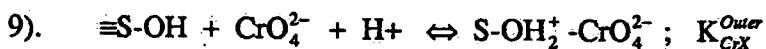
they affect the chromium concentrations in lakes remain an unexplored territory.

Sorption and Scavenging of Chromium

Although mineral solubility is likely to control the concentration of dissolved chromium in the pore waters of lake sediments, Cr concentrations within the water column are usually below the solubility limits of most Cr-bearing minerals. In sea water, scavenging by seston is an important mechanism controlling dissolved Cr concentrations (Murray, 1987; Jannasch et al., 1988), a feature that has recently been demonstrated in lake waters (Johnson et al., 1992; Balistrieri et al., 1992). Chromium, in its various forms, can bind to colloidal or particulate organic matter, hydrated Fe, Al or Mn oxides, clay particles, or plankton and other organisms (Jackson et al., 1980; Davis and Leckie, 1980; Hiraide and Mizuike, 1989). Adsorption unto suspended particulates can be described adequately using the diffuse double layer and constant capacitance models (see Rai et al., 1988; 1989 for an excellent discussion of Cr adsorption mechanisms). The adsorption of Cr species onto the inner-sphere of a seston with a variable charge can be represented by the following complexation reaction:



where $\equiv\text{S-OH}_2^+$, $\equiv\text{S-OH}^0$, and $\equiv\text{S-O}^-$ represent particulate surfaces and $K_{\text{Cr}}^{\text{inner}}$ and $K_{\text{CrX}}^{\text{inner}}$ are the intrinsic formation constants for the surface complexes. The outer-sphere complexation mechanisms can be represented by:



At equilibrium, the extent of retention of a chromium species can be derived for the inner sphere complexation:

$$11). \quad K_{CrX}^{inner} = \frac{[\equiv S - CrO_4^-]}{[\equiv S - OH^o][CrO_4^{2-}][H^+]} \exp(\Psi_i F / RT)$$

where Ψ_i is the electrical potential at the charged surface. For the outer sphere reaction, the expression becomes:

$$12). \quad K_{CrX}^{outer} = \frac{[\equiv S - OH_2^+ - HCO_4^-]}{[\equiv S - O^-][HCrO_4^-][H^+]} \exp(\Psi_i F / RT)$$

The equations show that the adsorption of either chromium species is pH dependent, but whereas the retention of Cr(III) increases with pH (Figure 5), the adsorption of Cr(VI) (exemplified by CrO_4^{2-}) decreases with pH (Figure 6). In addition, the adsorption capacity is dependent on the concentration of surface sites and the value of the surface complexation constant. Table 2 shows the intrinsic outer-sphere adsorption constants for CrO_4^{2-} and $HCrO_4^-$ for various surfaces. In general, the equilibrium constants match the adsorptivity sequence, Fe oxides > Al oxides > clays (Figure 5), and point to iron oxides and hydroxides as being particularly effective scavengers for Cr(III) in acidic to neutral lakes (Rai et al., 1988). Sorption by Mn oxides is often less important (Chuecas and Riley, 1966).

In the presence of competing ions like SO_4^{2-} or $H_4SiO_4^0$, the sorption of chromate has been shown to decrease dramatically (James and Bartlett, 1983; Zachara et.al., 1987). Many dissolved organic compounds contain negatively charged phenolic and carboxylic acid functional groups and hence can also compete against the chromate ions for adsorption sites. Many inorganic particles are coated with an organic film which can change the surface properties (Balistrieri et.al., 1981; Johnson and Xyla, 1991). This effect has been observed in lake waters, where goethite particles in the presence of varying concentrations of DOC (as low as 0.1 ppm) became negatively charged due to humic acid sorption (Tipping and Cooke, 1982). Also, Kerndorff and Schnitzer (1980)

found that at a pH of 5.8, 100% of the available Cr(III) was sorbed by a clay loam soil with 0.05-0.5 mM humic acid whereas in the absence of humic acid, over 50% of the chromium was precipitated as an unidentified hydroxide, suggesting that sorption and solubility processes do compete for available trace metals. Douglas et.al. (1986) and Nriagu et.al. (1983) studied the formation of Cr complexes within lake sediments and showed that sorption / complexation of Cr(III) with organic matter is an important process which can control dissolved Cr concentrations in pore water.

The strong role of adsorption/desorption on the distribution of chromium in lakes is well established. Jackson et al. (1980) reported that about 40-60% of the $^{51}\text{Cr(III)}$ added to softwater lakes in the Experimental Lakes Area (ELA) of northern Ontario was removed by chemisorption onto $>0.45 \mu\text{m}$ seston in only 20 days. The half-time for the removal of chromium from the water column was about 11 days in control lakes and 6.5 days in an experimentally acidified lake. Analyses of the NaOH extracts of the sediments and their Sephadex eluates suggested that the Cr was sorbed primarily to peptized colloidal hydrated ferric oxides. From studies using radioactive isotopes, Santschi (1988) obtained a rate constant of about 0.02 day^{-1} for sorptive removal of $^{51}\text{Cr(VI)}$ and a much higher rate for $^{51}\text{Cr(III)}$. The depletion of Cr(VI) in the hypolimnion of Lake Greifensee in Switzerland was similarly attributed to scavenging removal by seston with the rate constant estimated to be 0.005 day^{-1} (Johnson et al., 1992).

The adsorption of Cr(III) by Raisin River sediments (going into Lake Michigan) was found to be linear with a 48-hr adsorption density of about $6000 \mu\text{g/g}$ and a sediment-water partition coefficient of 30 L/g (Young et al., 1987). The desorption of the Cr was incomplete after 24 days and the irreversible sorption/desorption of Cr was attributed to kinetic constraints or to the precipitation of Cr and Fe oxyhydroxides. The adsorption/removal of chromium on mineral surfaces is probably more complex and can entail (i) the adsorption of Cr(VI) on the seston surface, (ii) the reduction of the Cr(VI)

followed by sorption or precipitation of the Cr(III), (iii) the complexation or sorption of the formed Cr(III) by organic ligands/matter (Masscheleyn et al., 1992). Pettine et al. (1992) showed that the particulate Cr concentrations in Po River (Italy) were strongly correlated with suspended matter ($r=0.93$), and particulate iron ($r=0.8$), aluminum ($r=0.81$) and magnesium ($r=0.76$) concentrations.

Sediments provide additional evidence for sorptive removal of Cr from the water column. Cahill and Shimp (1984) found a strong correlation between Cr and the organic carbon ($r=0.81$) and 2 μ m clay ($r=0.54$) contents of Lake Michigan sediments. A significant correlation ($r=0.69$) was reported between HCL-extractable Fe and Cr in surficial sediments of western Lake Erie (Lum and Gammon, 1985). In the Bay of Quinte sediments (Lake Ontario) with 6-71% organic matter, about 15-43% of the chromium was associated with organic matter and 5-15% with metal oxides (Ajayi and VanLoon, 1989). The predominant association of Cr with Fe/Mn/Al oxyhydroxides and organic matter has been reported in many polluted sediments including those of Lake Huzenbachersee in Germany (Steinberg and Hogel, 1990), River Nile (Elsokkary and Muller, 1990), Huang-Ho and Rhine Rivers (Hong and Forstner, 1983), Axios and Aliakmon Rivers in Greece (Samanidu and Fytianos, 1990), Gulf of Maine (Mayer and Fink, 1980), and the Dalhousie and Belledune Harbours, Nova Scotia (Samant et al., 1990). These studies, based on the use of various extracts to remove the chromium, suggest that most of the chromium is sorbed onto the oxide or organic fraction rather than held in the mineral lattice.

Oxidation/Reduction of Chromium

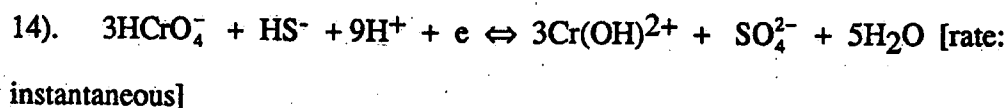
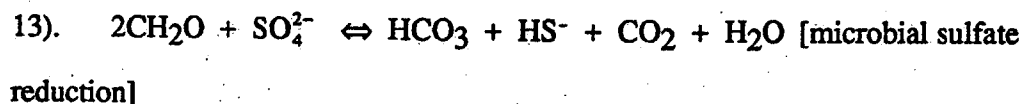
Electron transfer in chromium redox reactions is limited by the slow water exchange (Burgess, 1992), high redox potential (Rai et al., 1989), as well as the transition from tetrahedrally to octahedrally coordinated species (Murray, 1983). Although the

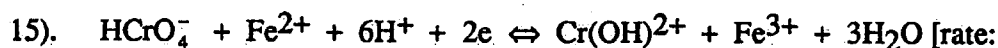
redox reactions often occur through the formation of chromium species with intermediate oxidation states, and rate laws have been determined showing the formation of Cr(V) and Cr(IV) to be the rate-limiting steps (Palmer and Wittbrodt, 1991), the reactions described in this report depict only the sum of all the steps. Any Cr(V) and Cr(IV) formed can remain in solution for up to one day (Boyko and Goodgame, 1986) but since both species are strong oxidants, they are likely to react fairly rapidly with relatively inert reduced complexes (Kieber and Helz, 1992).

Chromium reduction in sediments

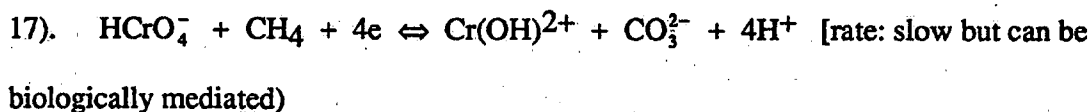
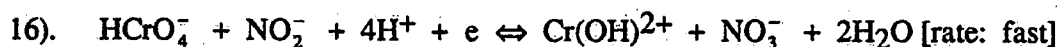
Chromate ion is a strong oxidizing agent and can be reduced easily in anoxic sediments or organic ooze at the bottom of some lakes, in anoxic hypolimnetic waters during stratification in some lakes, during groundwater flow prior to discharge into the lake, and possibly as an endogenic biological process (Kieber and Helz, 1992). In near neutral solutions, the approximate redox potential (Eh value) for the $\text{HCrO}_4^-/\text{Cr}(\text{OH})_2^{2+}$ couple of 1.3 V is higher than those for $\text{NO}_3^-/\text{NH}_4^+$ (~ 0.9 V), $\text{Fe}^{3+}/\text{Fe}^{2+}$ (~ 0.7 V), humic acid (~ 0.7 V), fulvic acid (~ 0.5 V), $\text{SO}_4^{2-}/\text{HS}^-$ (about -0.7 V), $\text{CO}_2/\text{CH}_2\text{O}$ (about -1.7 V). All these reaction couples can therefore reduce Cr(VI) under favorable circumstances. By contrast, the higher redox potential for $\text{MnO}_2/\text{Mn}(\text{II})$ couple (~ 1.8 V) is consistent with the observation that Mn(II) rarely reduces Cr(VI) in aqueous environments (Palmer and Wittbrodt, 1991).

Simplified reactions showing the reduction of Cr(VI) by sulfate reduction, Fe(II), NO_2^- , and CH_4 are shown below along with the rates of the reaction.

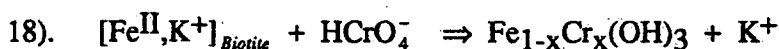




instantaneous]



Both sulfide and sulfite ions formed in eq (14) can reduce Cr(VI) with the former requiring Fe(II) as a catalyst. In lake sediments, most of the sulfur is bound to ferrous iron (Nriagu and Soon, 1985), which can reduce the chromium itself. The Cr(III) and Fe(III) formed from eq (15) may hydrolyze, combine and coprecipitate (see below). High concentrations of PO_4^{3-} would encourage the removal of Fe(III) by the precipitation of insoluble $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (strengite) and hence can speed up the reaction. Ferrous iron bound to mineral phases in sediments such as hematite, biotite and chlorite have also been shown to be effective in reducing Cr(VI) (Eary and Rai, 1988). The reaction apparently occurs in solution rather than on the mineral surface, implying that the rate of Cr reduction is determined by the rate of dissolution of the mineral phase. The schematic reaction



suggests that Cr reduction can affect the stability and composition of Fe(II)-containing clay minerals in lacustrine sediments.

Many naturally occurring and industrially produced organic compounds, including alcohols, phenols, carboxylic acids, proteins, cresols, etc, can reduce Cr(VI) effectively. Since the reduction of Cr(VI) by natural organic matter in soils is a first-order reaction (Amacher et al., 1988), the amount of reduction of dichromate by soils has been used as a measure of the soil organic carbon content (Nelson and Sommers, 1982); this low cost analytical technique needs to be applied to lake sediments. A large fraction of the organic matter in sediments is in the form of humic and fulvic acids which are effective Cr(VI) reducers (Palmer and Wittbrodt, 1991). Reduction of Cr(VI) by the

sugar-like molecule d-galacturonic acid (produced by pectic substances on plant roots) in acidic solutions (~ 4.2) occurs only if Cu(II) or Cr(III) is present to catalyze the reaction (Deiana et.al., 1991).

Bacterial reduction of Cr(VI) can be quite important in lake sediments. Most research in this area has been conducted with the goal of developing bacterial strains that could be used to detoxify polluted waste waters (Beveridge and Doyle, 1989; Cervantes, 1991). Natural strains do exist that have the capability to reduce Cr(VI). These species include the anaerobic species *Pseudomonas dechromaticans* and *Aeromonas dechromatica*, and the aerobic species *P. putida* (Cervantes, 1991). There is no reason why many other heterotrophic bacteria that use nitrate, sulfate and carbonate as electron acceptors in their metabolic processes cannot also do the same with chromate, resulting in a decromification process (Bartlett, 1991). Recent studies suggest that instead of reducing Cr(VI) indirectly through the production of sulfide, some of the sulfate reducing bacteria can reduce the Cr directly by an enzymatic mechanism (Coleman et al., 1993). Many enzymes are known to reduce Cr(VI) (Nieboer and Jusys, 1988) but their prevalence in the environment needs to be confirmed.

The oxidation/reduction processes described above control the cycling of Cr in lake sediments in the following manner: (A). Hexavalent Cr is unlikely to persist in the anaerobic sediments found below the oxidized microlayers which characterize most lakes. Indeed, Saleh et al. (1989) showed that a slurry containing only 10% of an anaerobic lake sediment reduced Cr(VI) instantly. (B). Most of the reduction reactions (above) generate alkalinity (consume protons) hence in softwaters, chromium pollution would tend to mitigate the effects of acid rain. (C). There is a geochemical decoupling of the Cr cycle from those of iron, manganese and other redox-sensitive elements. While Fe and Mn form mobile reduced species in anaerobic sediments and hypolimnion, the chromium is easily immobilized as Cr(III) as oxyhydroxides. In meromictic lakes and lakes that develop bottom anoxia during stratification, the sediments represent an

important source of Fe, Mn and associated metals but would be a sink for Cr(III). The converse should be expected in oligotrophic lakes. (D). The forms of Cr in sediments represent a potential indicator of the cultural influences on the lake ecosystem. In the natural environment, most of the Cr in sediments would be associated with detrital minerals derived from the weathering of rocks in the drainage basin (Gibbs, 1977; Loring, 1979; Sager et al., 1990). An increase in the input of Cr pollution or in the eutrophication of the water body would orchestrate the immobilization of Cr(III) resulting in the enhanced accumulation of Cr in the oxyhydroxide and organic fractions. Several studies have demonstrated such changes. Elsokkary and Muller (1990) showed that the residual fraction accounted for nearly 60% of the total Cr in slightly polluted River Nile sediments compared to about 20% in the highly polluted sediments. Steinberg and Hogel (1990) presented changes in profiles of the different forms of Cr in Lake Huzenbachersee sediments which was closely correlated with the history of industrial development in the drainage basin.

Chromium reduction in the water column

In anaerobic waters, Cr(VI) reduction would be dominated by the reduced species released from the sediments or by resuspended sediment particles. The Eh at which the reduction occurs remains equivocal, however. Johnson et al. (1992) observed high concentrations of Cr(VI) in anoxic hypolimnetic waters and concluded that Cr(VI) reduction is possible under strongly reducing conditions where sulfate reduction can occur. Masscheleyn et al. (1992) likewise found that Cr(VI) in floodwater of wetland soils was not reduced at Eh of 460 mV and pH 7.3 where Cr(III) is predicted to be thermodynamically stable. It would therefore appear that suspended particles and their surfaces are more important than thermodynamic equilibrium processes in Cr(VI) reduction in lakes. Several studies have indeed noted that Cr reduction in soil and sediment mixtures is strongly dependent on solid-to-solution ratio (Saleh et al., 1989;

Eckert et al., 1990; Masscheleyn et al., 1992).

The reduction of Cr(VI) to Cr(III) by organic matter in soils and sediments, especially by the humic and fulvic acids, has long been documented in the literature (James and Bartlett, 1983; Saleh et al., 1989; Masscheleyn et al., 1992). One of the first to address Cr(VI) reduction by DOC in sea water was Nakayama et al. (1981c), who observed approximately 90% reduction of 10 nM Cr(VI) with 5 micrograms of humic acid under natural pH conditions (7.5-8.2). Eckert et al. (1990) studied the many factors that affect the rate of Cr(VI) reduction by DOC, including the temperature and pH of the solution, the concentrations of the reactants and the intensity and wavelength of light present as well as the presence of catalysts and the labile nature of the DOC. They showed that the Cr(VI) reduction proceeded faster under field conditions than in a synthetic medium (pseudo first-order rate constant of 0.6 h^{-1} vs. 0.2 h^{-1} respectively) due to either more labile DOC or the presence of catalysts in the natural system. Stollenwerk and Grove (1985) noted a decrease in the concentrations of Cr(VI) in water samples preserved by standard techniques and that the rate of reduction increased with increasing NO_2 , DOC, H^+ and temperature. They showed that the addition of fulvic acid to an acidified groundwater sample resulted in complete loss of Cr(VI) within 5 days of storage at 25°C .

Direct photoreduction of Cr(VI) finds application in photographic plates which contain mixtures of Cr(VI) and organic sols such as gelatin (Kieber and Helz, 1992).

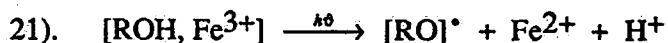
The reaction is generally believed to involve initial formation of a ligand-to-metal charge-transfer (LMCT) excited-state complex:



ROH refers to an alcohol functional group, HO_2^* is a superoxide radical and $[\text{RO}]^*$ and RO_2^* are radical groups. Potentially, this type of reaction may also be important in the oxidation of natural and synthetic organic molecules in surface waters (Zepp et al., 1992;

Pignatello, 1992; Sun and Pignatello, 1993). Photochemical reactions between DOC and Cr(VI) have been investigated by Riedel (1985) and Waite (1988). For DOC related reduction of Cr(VI), two pathways have been suggested. First, near UV photolysis was found to greatly increase the amount and rate of Cr(VI) reduction under acidic conditions (Waite, 1988). Second, in the presence of glycine, charge transfer irradiation of HCrO_4^- has been shown to cause the formation of Cr(V). This reaction is pH independent when HCrO_4^- is the absorbing species.

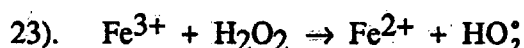
Domenech and Munoz (1990) showed that 30-70% of the Cr(VI) in neutral to alkaline solutions can be reduced on ZnO. Because ZnO is unlikely to be a common phase in lakes, other more abundant photochemical initiators such as nitrate, nitrite, organic matter and iron oxides and hydroxides are more likely to be involved in the photoreduction. In particular, several studies have documented the formation of Fe(II) during the photolysis of ferric compounds in the presence of organic ligands yields ferrous iron (Collienne, 1983; Waite and Szymczak, 1993b):



The Fe^{2+} so produced has been shown to rapidly reduce Cr(VI) even in air-saturated systems (Eary and Rai, 1988; Palmer and Wittbrodt, 1991; Kieber and Helz, 1992). The Cr(III) may then combine with any ferric ions present to form a hydroxide solid solution:



The importance of indirect photoreduction of Cr(VI) was recently demonstrated by Kieber and Helz (1992) who reported that the diurnal changes in the Cr(VI)/Cr(III) ratios of Black River, Maryland was due primarily to Cr(VI) reduction by photochemically derived Fe^{2+} . Photolysis of natural and organic compounds in lakes often yields H_2O_2 (and the superoxide anion, HO_2^\bullet ,) which is also able to reduce both Fe(III) and Cr(VI) especially under acidic conditions (Cooper et al., 1988; 1989; Kieber and Helz, 1992; Waite and Szymczak, 1993a):

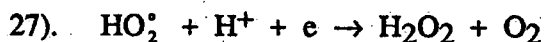
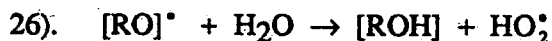




The Fe(II) from reaction 23 can participate in further Cr(VI) reduction while the hydrogen peroxide can be regenerated by the dismutation of the superoxide radical:



or by the Dorfman reaction (Sun and Pignatello, 1993):



The exact roles of these species in determining the fate chromium in lakes remain unclear at this time.

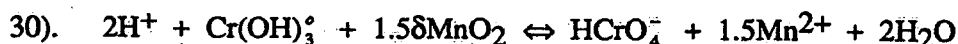
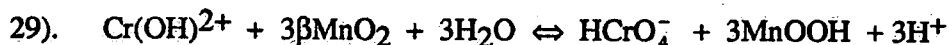
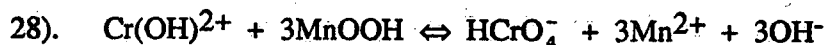
One can conclude from the preceeding discussions that significant reduction of Cr(VI) in the water column can be expected in humic and colored lakes and bogs with high dissolved organic carbon where photolytic reactions yield high concentrations ferrous iron, hydrogen peroxide, superoxide anion and LMCT complex. In clear water lakes, the sediments are likely to remain the primary foci for Cr(VI) reduction.

Oxidation of Cr(III)

Because of the high redox potential of the Cr(VI)/Cr(III) couple, there are very few natural oxidants in natural waters that are capable of oxidizing Cr(III) (Rai et.al., 1989). In addition, the oxidation kinetics are very slow with the calculated half-life for the transformation of Cr(III) to Cr(VI) in surface waters varying from 1 to 20 months (Schroeder and Lee, 1975; Cranston and Murray, 1980). The discussions below focus primarily on processes that are expected to occur in lake ecosystems and since they result in the undesirable formation of the more toxic Cr(VI) species, they the processes have been described in much greater detail.

Perhaps the most studied potential environmental oxidants for Cr(VI) are the various manganese oxides and oxyhydroxides. Johnson and Xyla (1991) claim that MnOOH is the most reactive manganese oxyhydroxide while Eary and Rai (1987)

maintain that BMnO_2 is the least reactive. Stoichiometric reactions for the Cr(III) oxidation by the Mn oxyhydroxides are shown below (see Eary and Rai, 1987; Johnson and Xyla, 1991; Fendorf and Zasoski, 1992), and the estimated rates are shown in Table 4.



In an aerobic environment, the reactive interfaces may be regenerated continuously as the Mn(II) produced is quickly reoxidized so that the role of Mn can thus be regarded as catalytic.

Johnson and Xyla (1991) suggest that three electrons are transferred stepwise via Cr(III) , Cr(IV) and Cr(V) as Cr(III) is oxidized by manganese oxides. Sorption onto, oxidation by and subsequent desorption of these intermediate compounds are all involved in the final production of Cr(VI) . The proposed mechanism is corroborated by Eary and Rai (1987) who showed that oxidation of Cr(III) by BMnO_2 was the same under both aerated and deaerated conditions, implying that the reaction is directly between Cr(III) and the Mn oxide, and that oxygen was not an intermediate phase or a catalyst. The rate of Cr(III) oxidation by Mn oxides is non-linear under acidic conditions (Eary and Rai, 1987). Factors that may affect the rate and extent of Cr(III) oxidation include the surface area and concentration of the Mn oxide, the pH of the solution, the concentration of Cr(III) (Fendorf and Zasoski, 1992), and the ionic strength of the solution (Van der Weijden and Reith, 1982).

An increase in the surface area of Mn oxide results in an increase in Cr(III) oxidation; the relationship is first order and the slope is close to unity (Johnson and Xyla, 1991; Eary and Rai, 1987). Surface area (and thus oxidation rate) may be reduced by reactions at the mineral surface, and such mechanisms have been proposed to explain the non-linearity of the oxidation reaction. Eary and Rai (1987) suggested that this effect

was due to the adsorption of the Cr(VI) produced onto the Mn surface. Fendorf and Zasoski (1992), however, pointed out that if sorption of the Cr oxyanions inhibits Cr(III) oxidation, then the rate of oxidation should decrease with decreasing pH due to surface protonation of the oxide; this effect was not observed. Recently, Masscheleyn et al. (1992) showed that a manganese and iron oxide film or layer floating on the floodwater surface was solely responsible for the oxidation of Cr(III) at their study site, and their results cast further doubt on what is known about the oxidation mechanism.

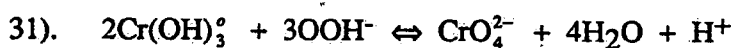
Pettine and Millero (1990) investigated the rate of oxidation as a function of pH. The relationship has a slope almost equal to unity, and thus for each unit drop in pH, the rate of oxidation also decreases by approximately an order of magnitude. As a result this relationship, Cr(III) oxidation may be much less pronounced in neutral to acidic lakes compared to ocean waters well buffered at pH = 8.2. At low pH, however, the dissolution of Mn oxides will compete with the oxidation reactions while at high pH, the precipitation of Cr(OH)₃ on the surface of the Mn oxide will limit the available reaction sites and hence slowing the rate of oxidation (Fendorf and Zasoski, 1992).

The effect of ionic strength has not been resolved. Schroeder and Lee (1975) state that the oxidation of Cr(III) by MnO₂ is greatly inhibited in filtered lake water compared to distilled water, due possibly to competition for sorption sites with Ca(II) and Mg(II). Contradicting this hypothesis, Johnson and Xyla (1991) conclude that the reaction with MnOOH is independent of ionic strength. It has been proposed that the rate of Cr(III) oxidation will be more rapid in freshwater due to lesser competition for sorption sites (Van der Weijden and Reith, 1982).

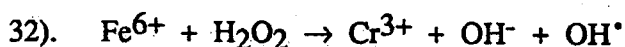
Numerous authors have examined the oxidation of Cr(III) to Cr(VI) by dissolved oxygen in well mixed surface waters. Eary and Rai (1987) observed no Cr(VI) formation when 19 mM Cr(III) was in contact with 8 ppm dissolved oxygen, Nakayama et.al. (1981c) reported no oxidation of 10 μ M Cr(III) with O₂ after 300 hours, while Van der Weijden and Reith (1982) detected no oxidation of 2 μ M Cr(III) after 6 weeks. Saleh

et al. (1989) estimated the half-life for Cr(III) oxidation by dissolved oxygen in several freshwater samples to be about 9 years. These studies point to the fact that even though the oxidation by O_2 is favoured thermodynamically, the kinetics are extremely slow, and the reaction can be considered to be environmentally unimportant.

In a number of recent papers, Pettine has proposed that H_2O_2 is the dominant oxidant for Cr(III) in natural waters (Pettine and Millero, 1990; Pettine et al., 1991; 1992). Baloga and Earley (1961) were, in fact, the first to show that low concentrations of H_2O_2 can readily oxidize Cr(III). Under alkaline conditions, the reactions can be represented schematically as follows:



In acidic systems, the reaction can be considered to be analogous to the Fenton reaction:

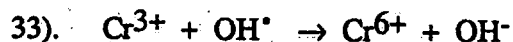


The calculations by Pettine and Millero (1990) actually suggest that such a reaction can control the Cr(VI)/Cr(III) ratios in the ocean. Using a concentration of 1.9 μM Cr(III) and 0.4 mM H_2O_2 , they derived a half-life of 24 days for Cr in the ocean (Pettine and Millero, 1990), but subsequently changed the figure to 45 days by considering the interactions Cr species with CO_3^{2-} and $B(OH)_4^-$ (Pettine et al., 1991). In the original paper it was stated that as low a concentration as 100 nM H_2O_2 could control the half-life of Cr(III). Whether the information regarding oxidation kinetics and speciation presented by Pettine et al. (1991) are applicable to lacustrine environments remains unclear at this time.

Pettine et al. (1991) have also proposed that Cr and B may combine to form mixed ligand complexes such as $Cr(H_2O)_5B(OH)_4^{2+}$ or $Cr(H_2O)_5-X(OH)_X[B(OH)_4]^{(2-X)+}$, and have suggested that these complexes may influence the kinetics of Cr(III) oxidation to Cr(VI) especially in environments containing appreciable concentrations of boron. They emphasized, however, that while borate does not seem to affect equilibrium Cr(III) speciation or solubility, it can influence the dynamics of chromium in natural waters.

Although Nakayama et.al. (1981b) also observed that borate ions decreased the recovery of Cr(III) with their coprecipitation technique, they provided no further insight on this observation. The addition of other elements can likewise effect the oxidation of Cr(III) by H_2O_2 , most notably Mg and CO_3^{2-} . High Mg concentrations (over $10^{-2.5}$ M) slowed the oxidation kinetics by strongly increasing the aging of Cr(III) while the addition of CO_3^{2-} did not affect the rate of oxidation but increased the rate of precipitation of solids compounds such as CrCO_3OH . (Pettine et.al., 1991). When spikes of Cr(III), B and H_2O_2 were added to natural seawater, the effect of B was much less pronounced, possibly due to the faster CO_3^{2-} precipitation kinetics (Pettine et.al., 1991). Addition of sulphate ions caused no observable effect.

One reaction pathway for the oxidation of Cr(III) that does not appear to have been examined in the literature is reaction with hydroxyl radicals, OH^\bullet . Hydroxyl radicals are extremely reactive transients that can oxidize most organic substances (Zepp et.al., 1992), and are among the strongest known environmental oxidants (Walling and Johnson, 1975; Zafiriou et.al., 1984). In natural waters, these radicals result from the photolysis of nitrate, ferric hydroxide complexes and H_2O_2 , and as a product of other photochemical reactions (Zepp et.al., 1992; Sun and Pignatello, 1993). A possible formation reaction for the hydroxyl radical has been given above, and its oxidation of Cr(III) can be depicted as follows:



Zepp et.al. (1992) showed that the production of OH^\bullet is quantitative over the pH range of 3 to 8 for Fe, and thus should occur readily in surface water environments containing adequate DOC, H_2O_2 , particulate ferric hydroxide and sunlight. The hydroxyl radical is extremely reactive, however, and numerous other species could scavenge it, such as H_2O_2 , Fe(II), Fe(III) and various organic ligands (Kieber and Helz, 1992).

The linkage between the iron and chromium cycles thus goes beyond the simple scavenging of chromium by particulate Fe compounds. Both iron and hydrogen peroxide

participate in several looped photochemical reactions which can result in either the reduction or oxidation of Cr in natural waters. These reactions reinforce the role of the surface microlayer in the cycling of chromium. Many lakes acquire a significant portion of their Cr budget from the atmosphere. The aerosols from high temperature combustion sources often contain large amounts of Cr(III) which can be dissolved by photochemical reactions upon entering the lake. The mobilization of Cr in the photic zone is a matter of significance to the aquatic biota with an essential requirement for chromium.

Biological Influence

Since chromium participates in the ocean biological cycle, its concentration should be positively correlated with the major nutrient elements, notably phosphate, nitrate and dissolved silica (Burton and Strathan, 1990). The available data suggest that Cr is better correlated with silica, suggesting that it is preferentially incorporated into the diatom frustules (Mayer, 1988). Pettine et al. (1992) reported a significant positive correlation between total dissolved chromium (Cr_t) and total dissolved phosphorus in Po River (Italy), the correlation equation being

$$34). \quad Cr_t \text{ (nM)} = 4.04 + 6.45 \mu\text{M PO}_4^{3-}; \quad r = 0.69$$

Few other studies have found any significant correlation between Cr and the nutrient elements in lacustrine environments, however.

As an essential element, chromium is bioaccumulated by a variety of organisms in lakes (Mance, 1987). The bioaccumulation factors (ratio of concentration in organism to that in water) for freshwater organisms range from 100 to over 120,000 in polluted waters (Jackson, 1988; Havas and Hutchinson, 1987). The Cr assimilated by an organism is reduced to Cr(III) within the cells so that the organic debris and remains are likely to be enriched in chromium. Particulate organic matter and fecal pellets are excellent scavengers for both Cr(III) and Cr(VI) in the water column (Jackson et al., 1980; Santschi, 1988). Intuitively, therefore, one would expect the Cr cycle to be

strongly influenced by biological processes in lakes. Unfortunately, most of the available databases on Cr concentrations in lakes have been compromised by contamination artifacts and the poor data quality has tended to mask any linkages between the Cr and biological cycles in lakes.

General Conclusions

The dominant physical and chemical processes that control the distribution and fate of Cr in various zones of given lake are shown in Figure 7. In general, the behaviors of trace metals in lakes can be classified into two principal categories: (a) conservatively behaved, and (b) particle dominated or scavenged. The concentrations of elements in group (a) are controlled primarily by proximity to pollution sources and by the mixing of waters with different levels of the particular trace element. They have high mean residence times in the water column because of the low geochemical reactivity. Group (b) elements are readily hydrolized and because they are highly particle-reactive, their residence time in water tends to be short. During the summer time, they may show a positive correlation with the biologically essential micronutrients, and their concentrations may be closely tied to the particulate organic matter driven by primary production in the lake.

Because of their geochemical characteristics, the two principal redox species of chromium fall into the two different categories defined above. In an oligotrophic lake, such as Lake Ontario, where Cr(VI) predominates (Beaubien, 1993, thesis in preparation), the profiles of dissolved Cr tend to remain constant or show slight features associated with atmospheric fluxes to the epilimnion or Cr removal in the nepheloid layer. The spatial distribution should also be uniform but with elevated levels expected near the major point sources and close to the major tributaries. Algal bloom may change the particulate-to-dissolved Cr ratios and can result in patchiness in both dissolved and

particulate concentrations especially in nearshore waters.

The contrasting geochemistries of Cr(III) and Cr(VI) are better demonstrated in meromictic lakes. Because of the permanent stratification, a build-up of Cr in the epilimnion can be expected because of atmospheric inputs and the photo-oxidation of aerosol-bound Cr(III) to Cr(VI) in the surface microlayer. The anaerobic hypolimnion, by contrast, should be marked by severe depletion of Cr due to the reduction of Cr(VI) to particle-seeking Cr(III). In anaerobic lakes that turnover in the spring and fall, a seasonal removal of chromium from the water often occurs but the Cr cycle is complicated by the development of oxidized sediment layers where any deposited Cr(III) is re-oxidized (see Johnson et al., 1992; Balistrieri et al., 1992). The combined effects of stratification and biogeochemical processes on the development of the various types of dissolved Cr profiles in lakes are shown in Figure 8.

The processes that determine the levels and distributions of the various Cr species are depicted in Figures 2 and 7. It shows the unique features of the chemistry of chromium which are unlike those of any other element. In contrast to Cr, both Fe and Mn are readily oxidized to insoluble and highly particle-reactive species and reduced to soluble reactive species. The interfaces serve different functions in the geochemistries of Cr, Fe, and Mn: oxidative dissolution of Cr occurs at the air-water interface while reductive dissolution typifies the sediment-water interface. The time-dependent processes at the interfaces and the slow kinetics of the redox-sensitive reactions often result in a departure from equilibrium conditions in the distribution of the various chromium species in lakes.

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FIGURE CAPTIONS

FIG. 1: Diagram showing the stability fields for the redox species of chromium under typical environmental conditions. From Palmer and Wittbrodt, 1991.

FIG. 2: Schematic diagram showing the dominant reactions, transformations and transport mechanisms involved in the geochemical cycling of chromium in lacustrine environments. The figure represents a period during thermal stratification, where the oxic/anoxic boundary has migrated from the sediments into the water column. Note that many of the reactions can occur in numerous parts of the system (as shown in Fig.7) depending upon local conditions.

FIG. 3: Plot showing the relationship between pH and the Cr(III) concentration as controlled by mineral solubility. The lines represent various mineral phases as calculated or measured by the authors indicated. After Saleh et.al., 1989.

FIG. 4: Figure showing the dependence of various metal chromate solubilities on solution pH. MINTEQA2 (Allison et.al., 1990) was used to generate the curves, assuming an initial solution of pure water and chemical equilibrium at 25°C.

FIG. 5: Percent Cr(III) sorbed onto the surface of hydrous ferrous oxide under the conditions shown as a function of pH. Figure shows the model fit by Dzombak and Morel (1990) of experimental data by Leckie et.al. (1984).

FIG. 6: Percent Cr(VI) sorbed as a function pH onto various mineral phases. Note the strong sorptive capacity of the various Fe oxides and oxyhydroxides in comparison to the other phases, and the circumneutral position of the sorption edge (From Rai et.al., 1988).

Fig. 7: Schematic diagram showing the various regions within a lake over which a physical or chemical process may dominate the cycling of chromium. The various boundary layers shown may or may not occur in any given lake, and relative positions may change with time. Note the large number and common overlap of the various mechanisms, implying the interaction of multiple processes.

Fig. 8: Schematic diagram showing total dissolved chromium concentrations as a function of depth within a thermally stratified lake. The four curves represent control of Cr concentration by the following mechanisms: (1) surface enrichment due to atmospheric input, river input, or photic or biological reactions; (2) depletion with depth due to scavenging of Cr by sorption to settling particles; (3) depletion of total dissolved chromium at depth within a strongly reduced environment due to the lower solubility of the reduced Cr(III) form relative to the oxidized Cr(VI) form; and (4) surface depletion and enrichment with depth due to the uptake of Cr by siliceous organisms. The figure assumes equilibrium conditions and that only one mechanism dominates each concentration profile.

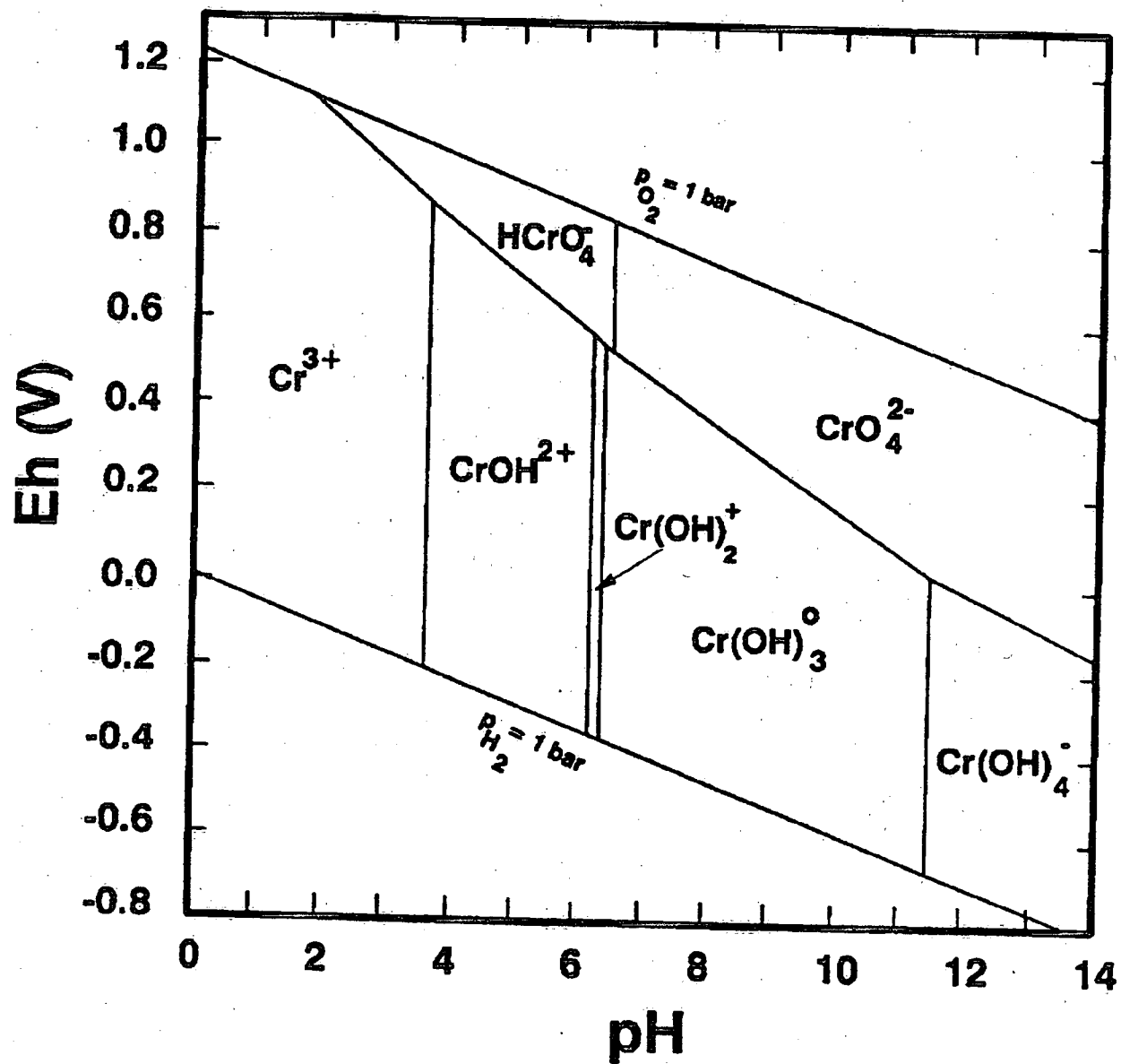


Fig. 1

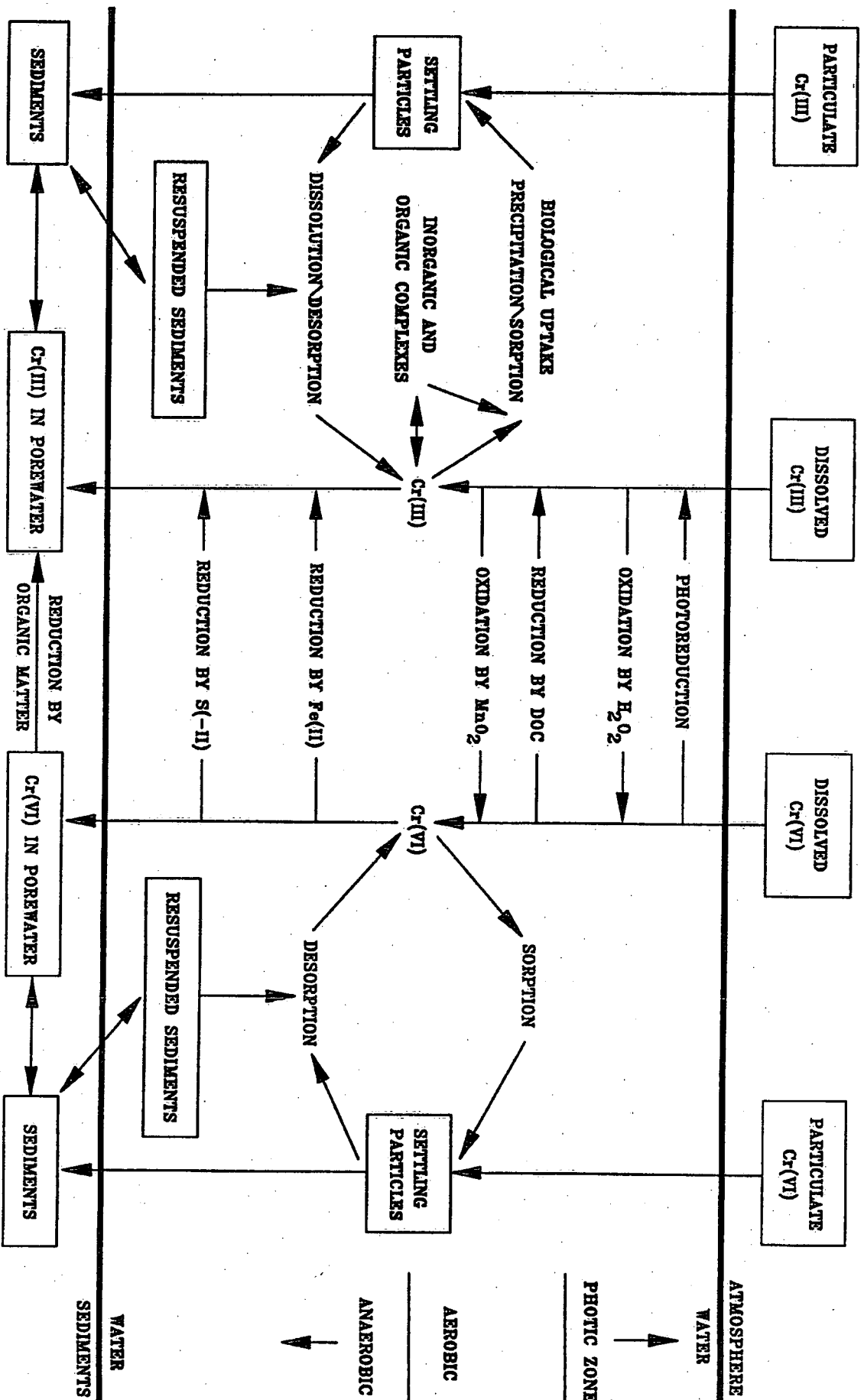


Fig. 2

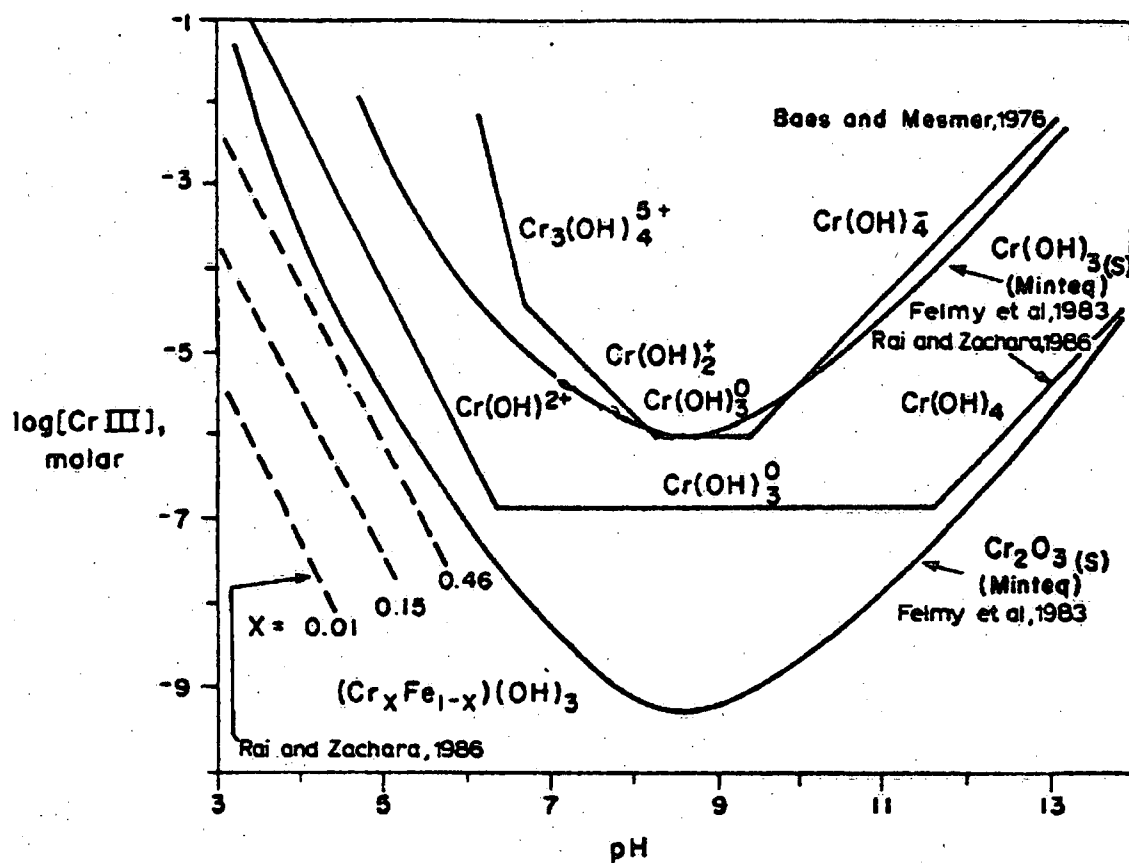


Fig. 3

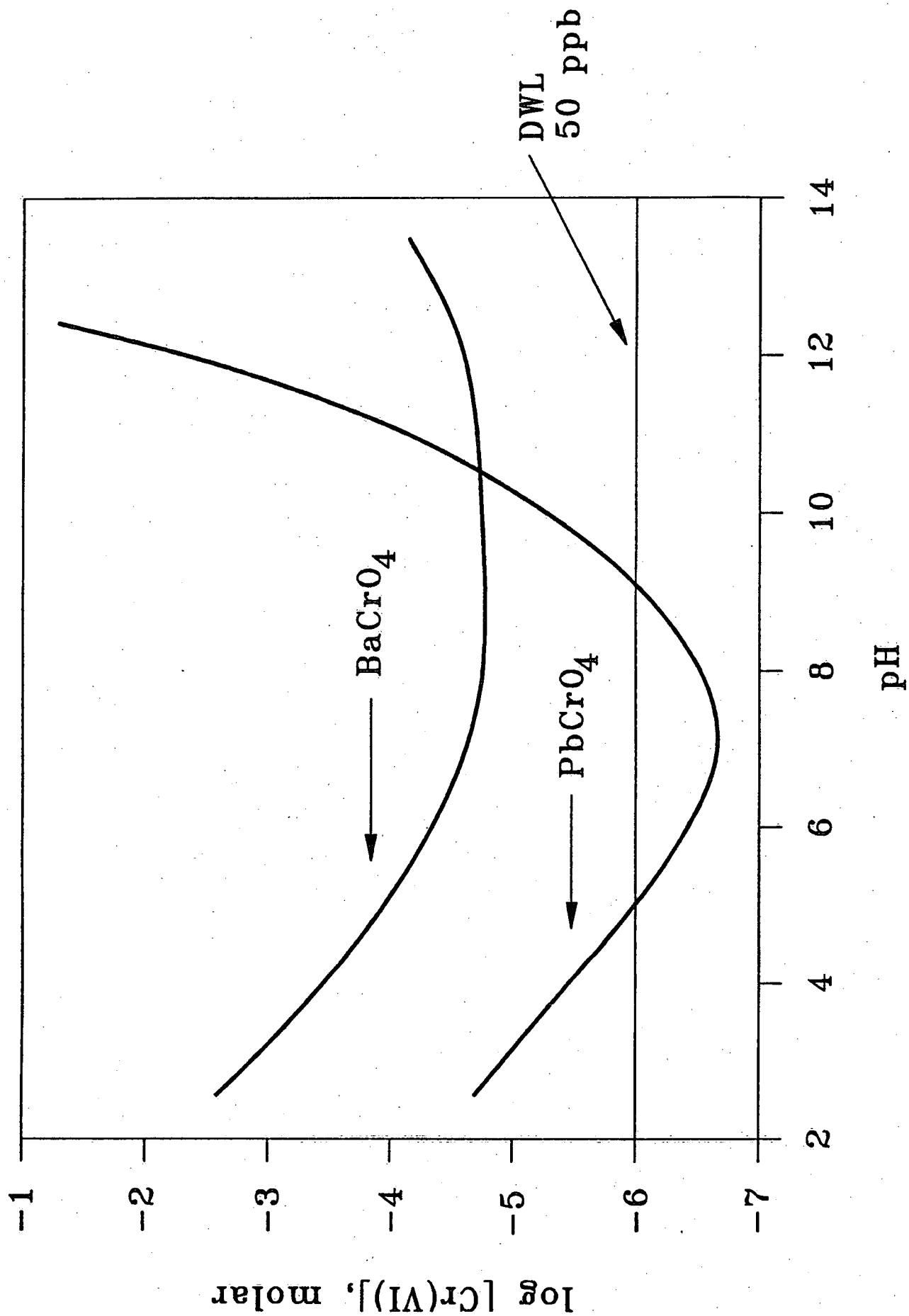
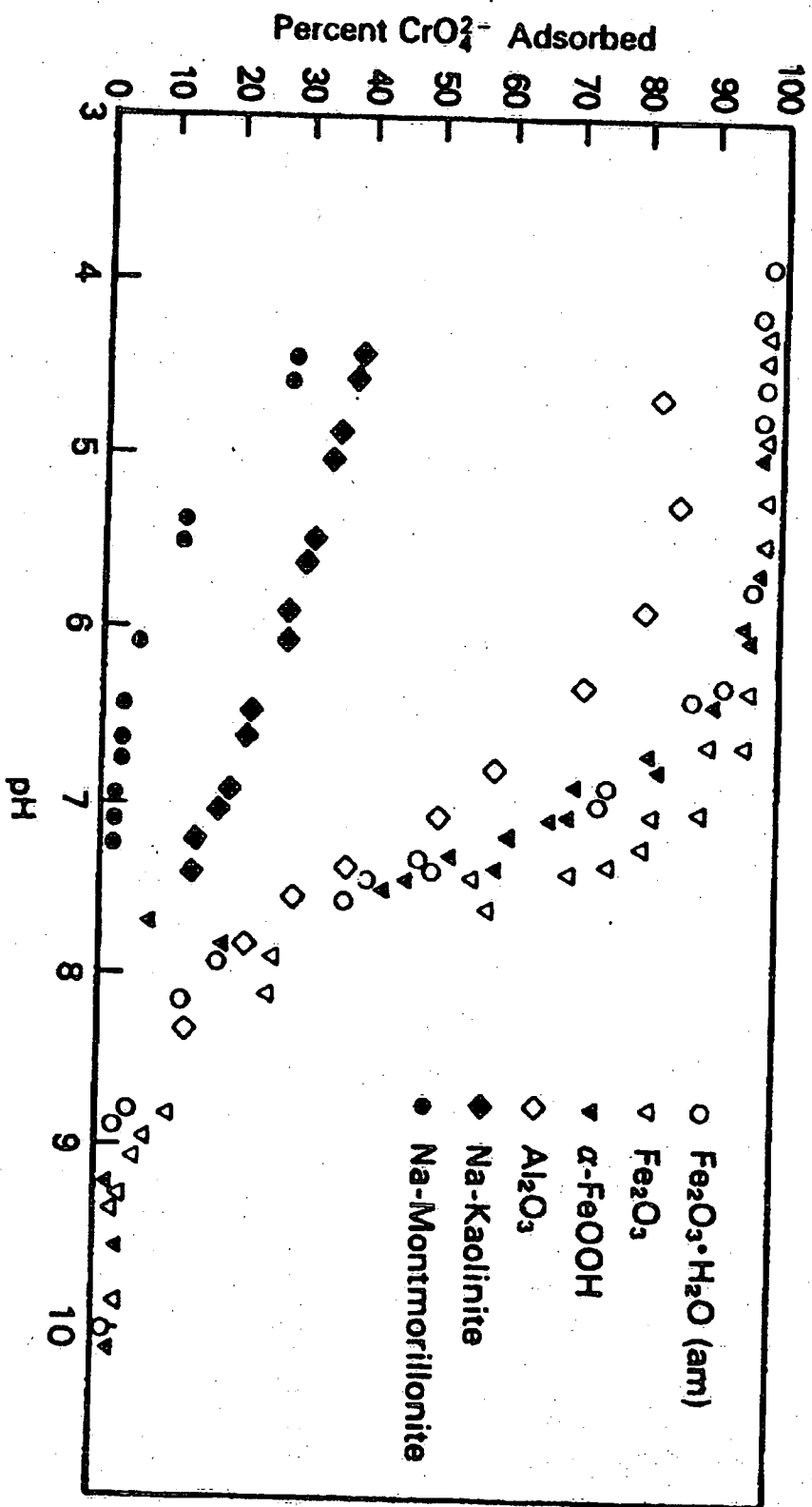


Fig. 4

Fig. 5



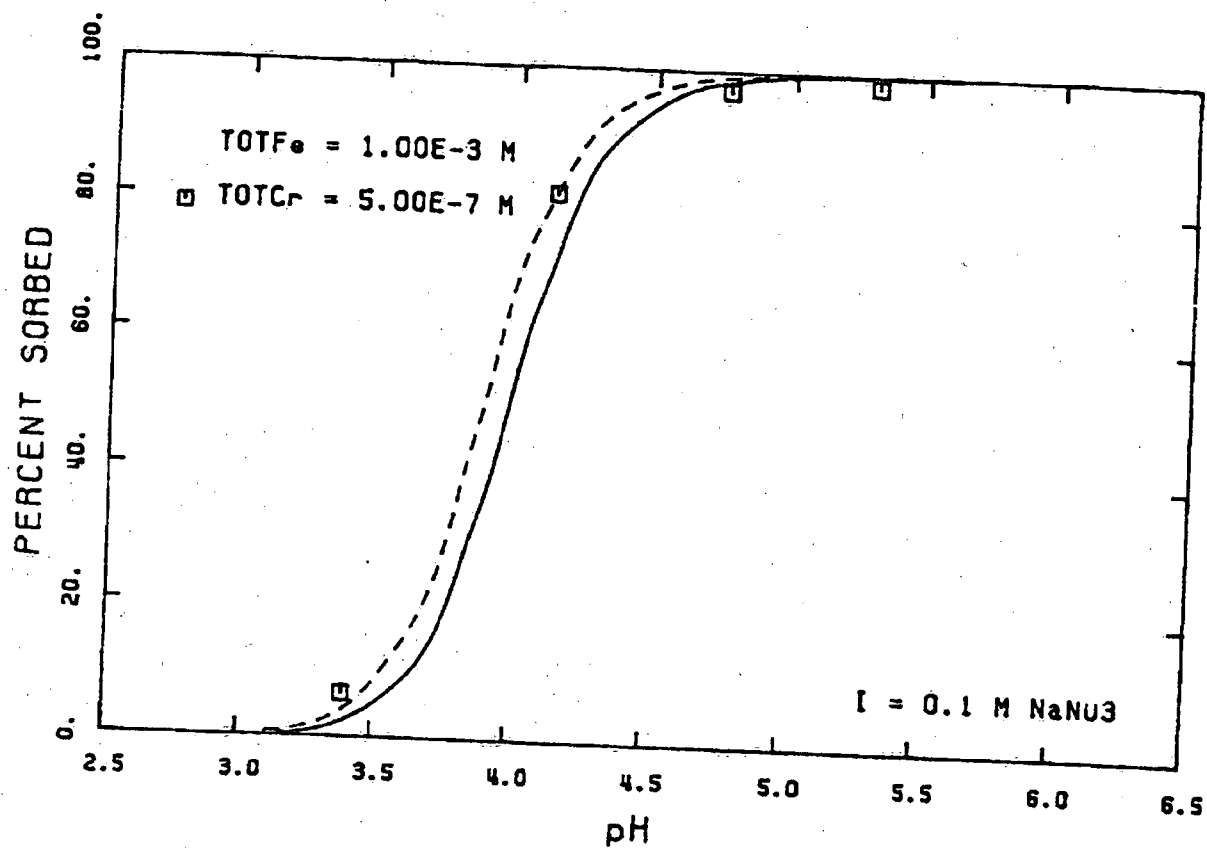


Fig. 6

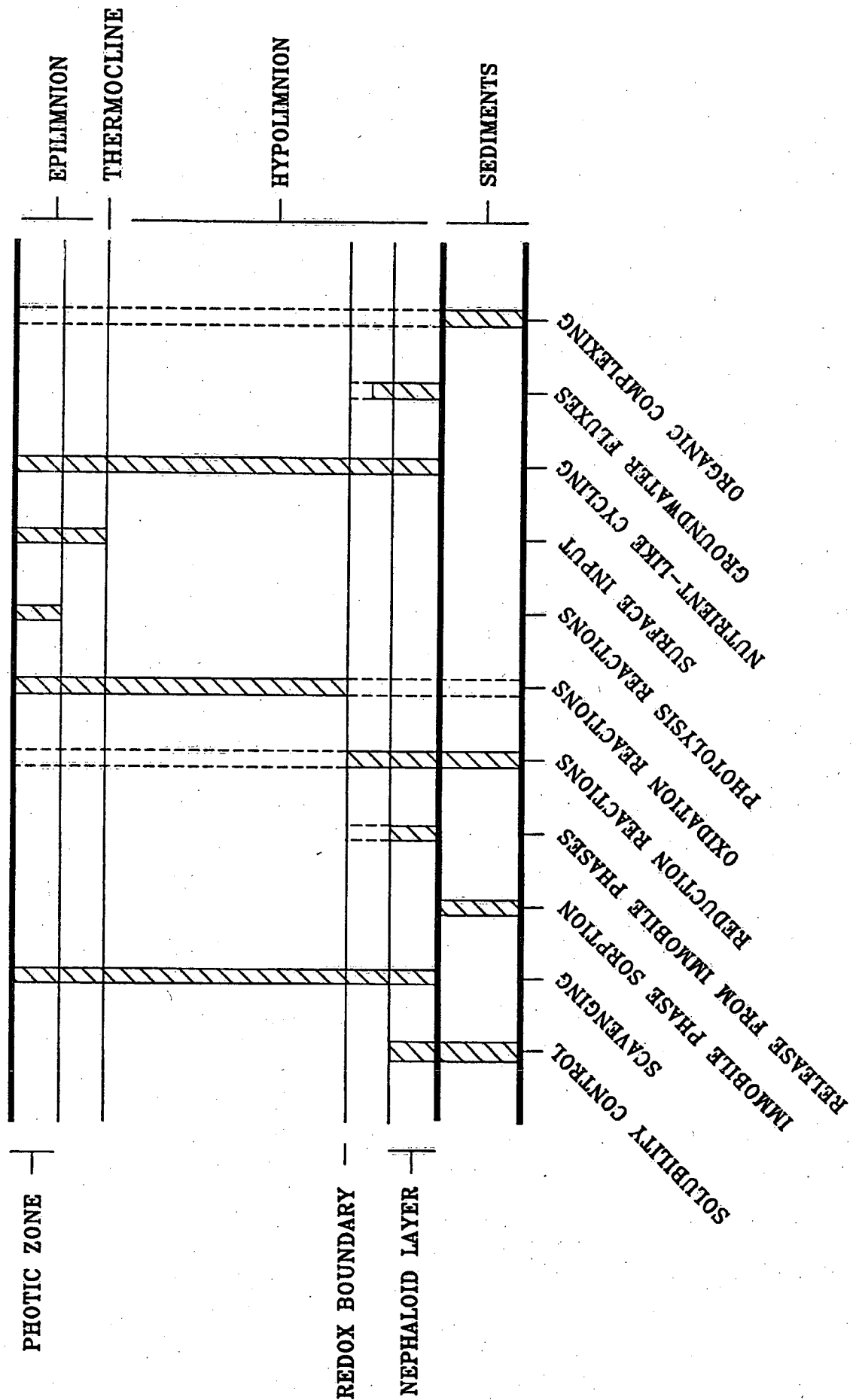


fig. 7

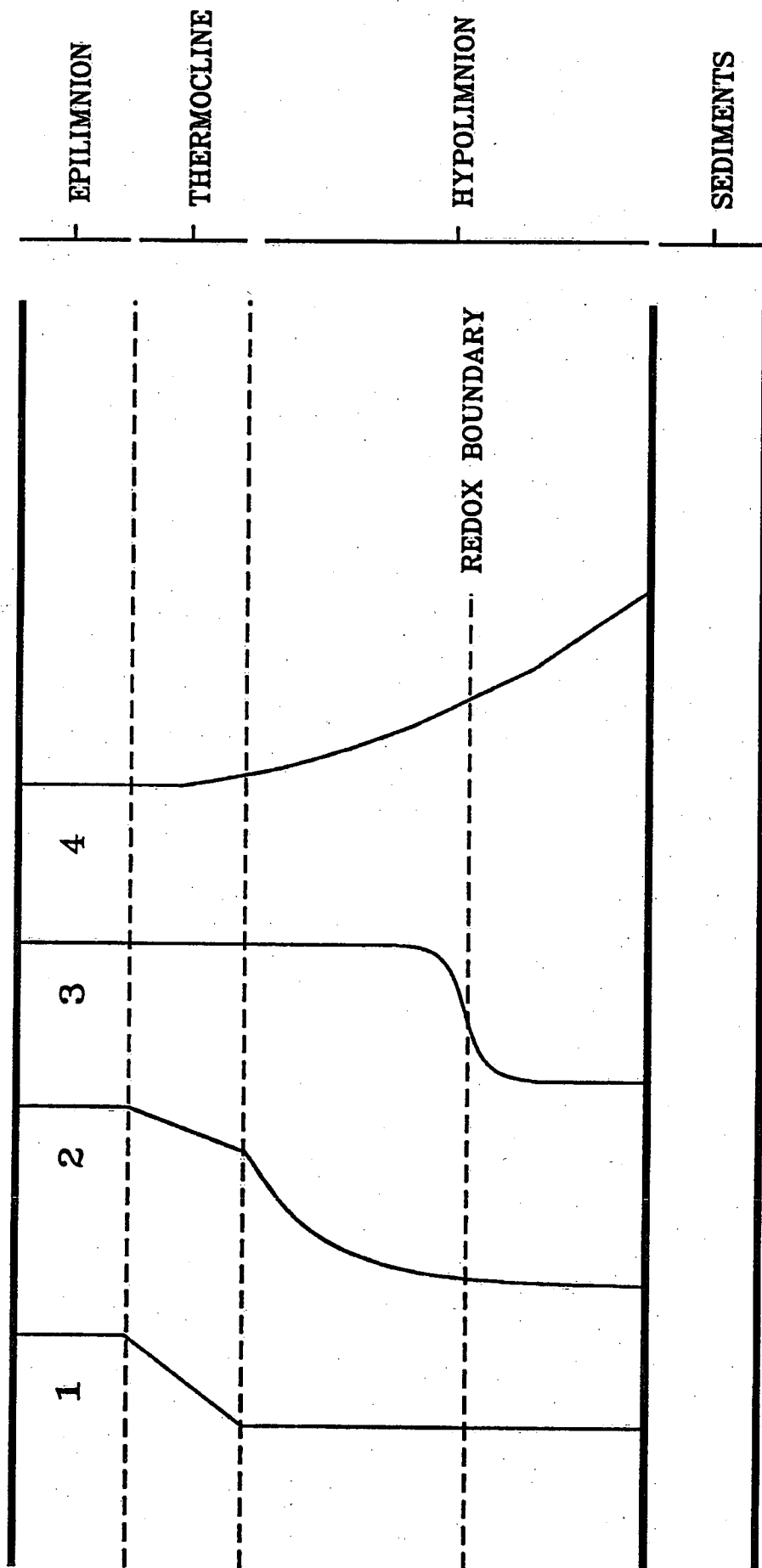


fig. 8

TOTAL DISSOLVED CHROMIUM (µg/L)							
MIN.	MAX.	AVG.	STUDY LOCATION	SAMPLING	SPECIATION	REFERENCES	
0.30	0.48	0.38	Lake Ontario (Canada)	Column	Yes	Beaubien et al. (unpub data 1991)	
0.20	3.20	0.60	Lake Ontario	Column	No	Neilson (1983)	
-	-	0.07	Lake Huron (1981)	Surface	No	Rossmann and Barres (1988)	
-	-	0.27	Lake Erie (1981)	Surface	No	"	
-	-	0.68	Lake Michigan (1981)	Surface	No	"	
-	-	0.08	Lake Superior (1983)	Surface	No	"	
-	-	0.71	Lake Ontario (1981)	Surface	No	"	
-	-	6.00	Bay of Quinte (Canada)	Surface	No	Poulton (1992)	
0.03	0.08	-	Lake Sammamish (USA)	Column	No	Balistreri et al. (1992)	
0.08	0.16	-	Greinfensee (Switzerland)	Column	Yes	Johnson et al. (1992)	

TABLE I. Values of total dissolved chromium in lakes globally. The concentrations measured vary widely, reflecting both the different pollution sources and local chemical processes occurring within the water column. Another factor that may contribute to this wide range is the analytical methods used. Note that very few of these studies sample with depth throughout the water column; of these, very few have examined the redox speciation of Cr.

Table 2. CHROMIUM REACTION EQUATIONS*

Reaction	Sorbent	Log K	Reference
$\text{SOH} + (\text{CrO}_4^{2-}) + \text{H}^+ \rightleftharpoons (\text{SOH}_2^+ - \text{CrO}_4^{2-})^-$	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$	10.1	Zachara et al., 1987
$\text{SOH}_2^+ + (\text{CrO}_4^{2-}) \rightleftharpoons (\text{SOH}_2^+ - \text{CrO}_4^{2-})^-$	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$	4.7	"
	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$	5.5	Davis and Leckie, 1980
	Fe_2O_3 (22 sites/nm ²)	6.11	Rai et al., 1988
	Fe_2O_3 (10 sites/nm ²)	6.74	"
	$\alpha\text{-FeOOH}$	5.6	"
	$\alpha\text{-Al}_2\text{O}_3$	5.84	"
	Kaolinite (6 sites/nm ²)	3.68	(Calculated from Honeyman, 1984)
	" (0.6 sites/nm ²)	5.21	Rai et al., 1988
$\text{SOH} + (\text{CrO}_4^{2-}) + 2\text{H}^+ \rightleftharpoons (\text{SOH}_2^+ - \text{HCrO}_4^-)$	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$	10.1	Zachara et al 1987
$\text{SOH}_2^+ + (\text{HCrO}_4^-) \rightleftharpoons (\text{SOH}_2^+ - \text{HCrO}_4^-)$	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$	7.5	"
	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$	6.5	Davis and Leckie, 1980
	Fe_2O_3 (22 sites/nm ²)	7.79	Rai et al., 1988
	Fe_2O_3 (10 sites/nm ²)	8.15	"
	$\alpha\text{-FeOOH}$	8.7	"
	$\alpha\text{-Al}_2\text{O}_3$	5.7	"
	Kaolinite (6 sites/nm ²)	4.42	(Calculated from Honeyman, 1984)
	" (0.6 sites/nm ²)	5.36	Rai et al., 1988

* From Richard and Bourg (1991).

NAME	FORMULA	pH _{zc} [†]	EXPERIMENTAL CONDITIONS	Cr(III) OX. RATE	EFFECT OF pH ON OXIDATION RATE	REFERENCE
Pyrolusite	βMnO ₂	7.3	pH = 3-10; [Cr(III)] = 1.9-38.5 (9.6) × 10 ⁵ M [MnO ₂] = 0.7-71.4 (35.6) m ² /L	10% in 100 hrs	decr. with incr. pH	Eary and Rai, 1987
Binnite	δMnO ₂	~2.3	pH = 3.8-7.9; [Cr(OH) ₃] = 10 mg/L [MnO ₂] = 50 mg/L pH = 3-5; [Cr(III)] = 33.5-770 (77) μM; [MnO ₂] = 0.1 g/L; [NaNO ₃] = 0.1 M	t _{1/2} = 1.95 yrs 4.5% in 50 hrs	---	Salch et al., 1989 Fendorf and Zasoski, 1992
Manganite	γMnOOH	~2.0	pH = 8.1; [Cr(III)] = 10 ⁻⁵ M; [MnOOH] = 30 mg/L; [Borate buffer] = 0.02 M	0.0008 M ⁻¹ s ⁻¹ †	---	Nakayama et al., 1981c
Unspecified	MnO ₂	---	pH = 3.5-9.5 (4.5); [Cr(III)] = 0.25-5.0 (0.5) μM; [MnOOH] = 0.11-0.57 (0.34) mM; [KNO ₃] = 0.001-0.1 (0.01) M; T = 4.1-25.0 °C	0.0108 L m ⁻² s ⁻¹	constant over exp. range	Johnson and Xyla, 1991
			pH = 8.3-8.7; [Cr(III)] = 125 μg/L; [MnO ₂] = 25, 100, 250 mg/L	1.34 M ⁻¹ s ⁻¹ †	---	Schroeder and Lee, 1975
			pH = 5.5-8.0; [Cr(III)] = 100 μg/L; [MnO ₂] = 100 mg/L	0.0063 M ⁻¹ s ⁻¹ †	---	Van der Weijden and Reith, 1982

TABLE III. Information regarding the various manganese mineral phases studied in the oxidation of Cr(III). † - Values from Healy et al., 1966; ‡ - Bold values are experimental conditions used for Cr(III) oxidation rate values; ‡ - Calculated values from Johnson and Xyla, 1991; t_{1/2} is the half life for Cr(III) oxidation in synthetic "hard water"; --- indicates not addressed in this study.

% Cr(VI)	% Cr(III)	% Cr _{org}	SAMPLE LOCATION	METHOD	REFERENCE
5 - 60	3 - 48	0 - 91§	Pacific Ocean (N. of Sydney, Australia)	Co precipitation	Ahern et al., 1985
95 ± 5	5 ± 5	N/M	Pacific Ocean (Cascadia Basin)	"	Cranston, 1983
< 50	> 50	N/M	Atlantic Ocean (N. Wales)	Differential	Elderfield, 1970
25	15	60	Pacific Ocean / Japan Sea	Co precipitation	Nakayama et al., 1981c
98	3	N/M	Mediterranean Sea (S. of Marseille, France)	Volametric	Boussemart et al., 1992
50	50	N/M	Atlantic Ocean (Britany, France)	Isotope dilution	Jéand et al., 1984
86	13	N/M	Mediterranean Sea (E. of Alexandria, Egypt)	Co precipitation	Aboul Dahab O., 1989
96	5	N/M	Saanich Inlet - oxic (Canada)	Co precipitation	Cranston and Murray, 1978
21	79	N/M	Saanich Inlet - anoxic (Canada)	"	Cranston and Murray, 1978
36	35	27	Harima-Nada (SW of Himeji, Japan)	"	Ozaki et al., 1991
4	38	57	Ito River (SW of Himeji, Japan)	"	"
77	15	8	Shonai and Kiso Rivers (Japan)	Ion exchange	Hiraide et al., 1989
50 - 68	12 - 24	10 - 24§	Georges, Cooks and Parramatta Rivers (Australia)	Co precipitation	Mullins, 1984
N/A	50	N/A	Susquehanna River (USA)	Ion exchange	Pankow et al., 1977
90	10	N/M	Columbia River (USA)	Co precipitation	Cranston and Murray, 1980
86	17	N/M	Po River (Italy)	Solvent extraction	Pettine et al., 1992
21	41	37	Sau Reservoir (Spain)	Co precipitation	Obols et al., 1987
100	~ 0	~ 0	Lake Greifen - oxic (Switzerland)	Ion exchange	Johnson, 1990f
41	~ 0	59	Lake Greifen - anoxic (Switzerland)	"	"
~ 100	~ 0	~ 0	Lake Greifen - oxic (Switzerland)	"	Johnson et al., 1992

Table IV. Percentages of the three major forms of dissolved Cr in oceans, rivers and lakes, measured using various separation techniques. Note the wide range in values, various methods used and paucity of lake water data. Single numbers represent averages unless otherwise stated. § - "bound chromium" defined as irradiated total dissolved Cr minus dissolved Cr(III) + Cr(VI) values; N/M - Not Measured; N/A - Not Applicable (ie method does not clearly separate out species); f - results are single samples.

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