

**THE GEOCHEMISTRY OF CHROMIUM IN VARIOUS MARINE
ENVIRONMENTS**

by

ROBERT K. MUGO

B.Sc. (Hons), The University of Nairobi, Kenya, 1987.

M.Sc., The University of British Columbia, 1991.

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Department of CHEMISTRY

The University of British Columbia
Vancouver, Canada

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Abstract

The geochemistry of chromium in different marine environments was investigated using a combination of laboratory and field studies. Chromium speciation and concentrations were determined using an electron capture detection gas chromatographic technique (ECD-GC) on samples from a broad range of environments. The distribution of this element in aquatic environments appears to be driven mainly by redox, sorption/co-precipitation and complexation processes.

Dissolved chromium profiles in the Pacific and Atlantic oceans and in two B.C. inlets show a slight surface depletion (10-25 %) and an increase near the sediment-water interface. The surface depletion might suggest Cr involvement in nutrient cycling in the oceans, but the lack of clear Cr-nutrients correlation in both oceanic basins and also the lack of an inter-ocean nutrient-type gradient suggests that other factors may be important. Photoreduction of Cr(VI) coupled with removal via sorption may be important controls on Cr speciation in surface waters. Nearshore areas showed enrichment in total dissolved Cr values relative to the open ocean likely through elevated inputs via riverine run-off. In addition, higher dissolved organic matter (DOM) concentrations in coastal areas can lead to higher Cr(III) values by reducing Cr(VI) (directly or through the Fe photochemical cycle) and via complexation of Cr(III), allowing this species to remain in solution in excess of levels predicted by thermodynamic equilibrium.

Chromium cycling in areas with redox gradients is controlled by speciation changes, sorption/co-precipitation and complexation processes. Under suboxic and anoxic conditions, Cr(VI) is reduced to Cr(III), much of which is either removed or is bound as non-labile colloidal Cr forms in solution. In Saanich Inlet, a seasonally anoxic fjord, more than 90 % of chromate is reduced to Cr(III) during stratification, roughly half of which is detected in either labile or non-labile forms; the rest is removed presumably via sorption and/or co-precipitation processes. In the Black Sea, a permanently anoxic basin, Cr(VI) is reduced to Cr(III) at the redox interface, this species subsequently undergoes removal onto particles and is released in deep waters where it is

stabilized by formation of organic and/or colloidal complexes. Cr residence time in the Black Sea interface zone is estimated to be ~ 40 yrs, much shorter than the ~ 1000 years calculated for the anoxic region where reduced Cr(III) species are quite stable.

Total chromium values in hydrothermal vents areas over the Juan de Fuca Ridge (JDFR) showed approximately a two-fold enrichment over values in the open Pacific Ocean. These preliminary results suggest that hydrothermal activity may be a source of Cr for waters at the JDFR. Total Cr in vent fluids is estimated to be at least 80 ± 10 nM based on Si data.

Laboratory studies of Cr transformations support field observations that processes such as Cr(VI) reduction, Cr(III) binding by DOM and sorption are important controls in regulating the distribution of Cr species in aquatic environments. Humic acids were shown to be capable of reducing Cr(VI) under a wide range of acidic pH conditions. They are also capable of binding Cr(III) in non-labile forms that require oxidative digestion before they can be detected by the ECD-GC technique. Preliminary results also showed that Fe(II) may be an even faster reductant for Cr(VI) in seawater, especially at higher pH typical of marine environments.

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GLOSSARY

DDI	distilled deionized water
ECD	electron capture detector
ft	foot (feet)
g	gram
GC	gas chromatography
GFAAS	graphite furnace atomic absorption spectrometer
HAc	acetic acid
HDPE	high density polyethylene
HEPA	high efficiency particle air (filter)
hr	hour
Htfa/tfa	1,1,1-trifluoro-2,4-pentanedione
in	inch
LDPE	low density polyethylene
min	minute
mL	milliliter
mm	millimeter
NaAc	sodium acetate
nM	nanomolar
o.d	outer diameter
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
RSD	relative standard deviation
salinity	grams of dissolved salts in one kilogram of seawater
sec	second

yr	year
θ	potential temperature
τ	residence time
$^{\circ}\text{C}$	degrees centigrade
μL	microliter
μm	micrometer

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Chapter 1

INTRODUCTION

1.1 Overview

Our knowledge of the distributions and chemical behavior of trace elements in natural waters has grown tremendously in the last two decades due to advances in trace metal clean conditions for sampling, storage and measurement, and the use of modern analytical methods and instruments. Progress in trace metal geochemistry has been charted through excellent periodic reviews (Burton and Statham, 1982; Bruland, 1983; Whitfield and Turner, 1987; Donat and Bruland, 1995). Reliable trace metal data has allowed the complex cycles of these elements to be understood leading to their use as tracers of various physical and biological processes in the oceans (e.g., Measures and Edmond, 1992; Coale and Bruland, 1985; Bacon and Anderson, 1982; Boyle, 1988).

Trace element distributions in natural waters are controlled by a combination of external inputs, internal cycling and removal processes, superimposed upon physical mixing and various biological and chemical transformations in the environment. The relative importance of a particular process will depend on the geochemical conditions of a system and the chemical characteristics of the elements. Trace metals can exist in aquatic environments in a number of chemical species. These species include different oxidation states, different physical forms (dissolved, colloidal, particulate) and complexes with inorganic and organic ligands. As our knowledge of the oceanic chemistry of various trace metals has advanced dramatically by virtue of improved total concentration data, it has become apparent that total concentrations alone are insufficient for deciphering the complex cycles and interactions of these elements. Trace metal geochemists continue therefore to develop new (and also adapt existing) analytical techniques for the determination of different species in aquatic systems. Knowledge of the concentrations of the various forms is extremely important because the different species can enter into very different biogeochemical interactions in the aquatic environment.

1.2 Research Objectives

Chromium exists in natural waters in two main oxidation states, Cr(III) and Cr(VI), both at sub-parts per billion (ppb) (low nanomolar) concentrations. The two oxidation states are characterized by very different properties and chemistries and are not easily measured without alteration and inter-conversion. The paucity and inconsistencies in the literature on Cr speciation data in aquatic environments can be attributed, in part, to the lack of a reliable analytical scheme for the determination of Cr species accurately and rapidly without alteration. In order to better understand the aquatic geochemistry of this environmentally-important trace element, what was therefore needed was: (1) a reliable and highly sensitive technique for Cr species determination and (2) to use the technique to measure Cr species in a variety of locations with variable chemical and physical conditions.

The development of an accurate and rapid electron capture detector gas chromatographic (ECD-GC) technique for the determination of chromium in seawater was the subject of a previous study (Mugo, 1991; Mugo and Orians, 1993). The focus of this dissertation was to apply the ECD-GC technique, in combination with other methods, to the study of the distribution, speciation, and geochemical behavior of Cr in various marine environments. The specific objectives of this work were:

- (i) to compare the depth distribution of Cr species in the Pacific and Atlantic oceans;
- (ii) to determine the concentration and speciation of Cr in various inlets of British Columbia;
- (iii) to assess the effect of environmental changes on Cr redox behavior;
- (iv) to study the geochemical cycling of Cr in a permanently anoxic basin;
- (v) to evaluate the effect of hydrothermal activity on Cr species distribution;
- (vi) to conduct laboratory studies of Cr species transformations and evaluate their potential impact on the Cr environmental cycle.

1.3 Thesis Organization

This dissertation is organized into six chapters. Chapter 1 (Introduction) presents an overview of trace element oceanic distributions and the basic processes controlling Cr aquatic chemistry. Chapter 2 describes the general methods and materials used in this study. Chapters 3, 4 and 5 are devoted to chromium distributions and geochemistry in the different study areas. Laboratory studies of Cr transformations are presented in Chapter 6. Chapters 3, 4, 5 and 6 are each written in a paper-type format intended for publication; as such, material present in Chapters 1 and 2 may be repeated. The appendix contains the raw data used for plots and graphs in the thesis.

1.4 Trace Element Oceanic Distributions

Trace element oceanic distributions represent a complex interplay between input and removal functions coupled with biological activity and physical mixing processes. The inputs may be from rivers, atmospheric deposition, sediments and hydrothermal activity. Removal processes can be via scavenging onto sinking particles, incorporation into biological phases, through redox changes and also via submarine hydrothermal activity. To understand the behavior of trace elements in the oceans, depth profiles (element concentration as a function of depth) are commonly used. Generally, depth profiles can be described as one or a combination of three principal types reflecting their biogeochemical interactions with particles: conservative, nutrient-type and scavenged (Figure 1.4.1).

Trace elements that show a constant concentration relative to salinity as a result of the low reactivity of the elements in seawater are termed "conservative". Examples of trace elements with a conservative-type distribution are Cs and Mo. These elements are removed only slowly from the oceans and have long residence times (defined as total amount of element in oceans divided by its supply or removal rate at steady state).

Reactive trace metals exist in low concentrations in seawater relative to their crustal abundance. Two sub-categories that fall in this class are "scavenged-type" and "nutrient-type" (or recycled). Scavenged trace metals (e.g. Al, Pb) undergo net removal onto particles in intermediate and deep waters as well as in the surface. They exhibit concentration maxima corresponding to their external sources and have deep water concentrations in the North Pacific that are less than those observed in the younger deep waters of the North Atlantic. Scavenged elements have short residence times, generally less than 1000 years.

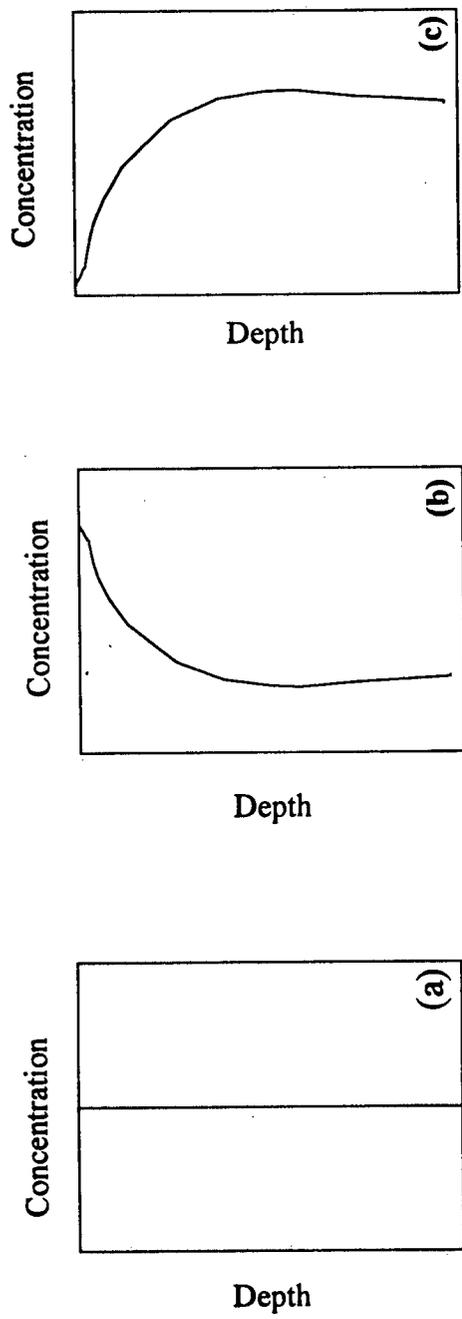


Figure 1.4.1 The three major distribution types for trace elements in seawater
(a) Conservative (b) Scavenged and (c) Nutrient types.

Nutrient-type (or recycled) elements exhibit surface depletion and enrichment in deep waters as a result of the involvement of the element in biological cycles, just like the major nutrients nitrate, phosphate and silica. This cycle results in removal of the element from surface waters by plankton and biologically produced particulate material and its subsequent regeneration into solution when the biological debris sinks and is oxidized or resolubilized. Nutrient-type elements, best exemplified by Zn and Cd, have concentrations in the relatively young waters of the North Atlantic which are substantially less than those observed in the older, nutrient-rich, North Pacific deep waters. They have a residence time in the oceans of between 10^3 - 10^5 years.

1.5 CHROMIUM

1.5.1 Introduction

Chromium was discovered in 1797 by French chemist Nicolas-Louis Vauquelin in the mineral crocoite (PbCrO_4). The name was selected from the Greek "chroma" for color, due to the many vividly colored compounds and minerals that are characteristic of Cr (Rollinson, 1973). Chromium (atomic number 24) is a first order transition metal with an outer shell electron configuration of $3d^5 4s^1$. The reported abundance in the earth's crust varies from 100 to 300 ppm. There are four naturally occurring isotopes of chromium: ^{50}Cr (4.35%), ^{52}Cr (83.79%), ^{53}Cr (9.50%) and ^{54}Cr (2.36%). In addition there are a number of radioactive isotopes of which the longest lived is ^{51}Cr with $t_{1/2} = 27.8$ days. Chromium can exist in the environment under several oxidation states ranging from Cr(0) (the metallic form) to Cr(VI). However, in the pH range of natural aquatic systems only the trivalent state, Cr(III) ($3d^3 4s^0$) and the hexavalent state, Cr(VI) ($3d^0 4s^0$) are important. These two ground states exist mainly in the octahedral ($^4A_{2g}$) and tetrahedral (1A_1) geometries, respectively. The toxicity, mobility and concentrations of chromium in different environments are dependent on its oxidation state.

Cr(III) has three 3d electrons. In octahedral coordination, these three electrons are in the high spin state and the crystal field stabilization energy is $6/5\Delta_o$, the largest octahedral-site preference energy available to transition metals (Burns, 1970). Cr(III) compounds are kinetically stable in keeping with the half-filled t_{2g} level of the d^3 configuration in octahedral geometry. This stable nature results in low solubility for Cr(III) minerals (Strubican and Greskovich, 1975). For example, the solubility product for $\text{Cr}(\text{OH})_3^0$ is on the order of 10^{-30} (Morel, 1983) and is even lower for solid solutions of chromite - $(\text{Fe}, \text{Cr})(\text{OH})_3$ (Rai *et al.*, 1989). The stable nature is also responsible for slow aqueous reactions for Cr(III) complexes e.g., the violet hexaquo species is inert to water exchange with $k = 3.5 \times 10^{-6} \text{ s}^{-1}$, i.e., a half-life of a few days (Hunt, 1963).

Cr(VI) ($3d^0$) forms a variety of oxospecies depending on pH and is only stable in oxygenated environments. Because of its large ionic potential, it is an extremely strong acid and the soluble tetrahedral chromate ion, CrO_4^{2-} is the common species.

1.5.2 Mineralogy

Chromium is a common crustal trace element found almost exclusively in ultrabasic rocks. It is thought that Cr minerals crystallize early from intrusive igneous masses due to the large stabilization energy for Cr(III) (Irvine, 1975). Major Cr bearing minerals found are chromite (45 % Cr), magnesiochromite (38 % Cr), stichtite (15 % Cr), and uvarovite (18 % Cr) (National Research Council of Canada Report, 1976). The only commercial source of Cr occurs as chromite. The Cr content of various natural solids is summarized in Table 1.5.2.1. Granite, carbonates and sandy sediments present the lowest Cr content whereas shales, river suspended matter and soils typically exhibit highest levels.

Cr mineralogy is dominated by Cr(III) species, whereas Cr(II) may be significant in minerals found on the moon or other strongly reducing environments. Cr(VI) is found in chromate minerals such as crocoite (PbCrO_4) which occur in the oxidized zone of lead-rich ores (Burns and Burns, 1975). Solid solutions of $\text{Ba}(\text{SO}_4, \text{CrO}_4)$ have also been reported (Rai and Zachara, 1988) presumably because of similar geometry of SO_4^{2-} and CrO_4^{2-} .

Chromium content (ppm)

Type of solid	Typical	Range
Lithosphere	125	78.0-198
Granite	20.8	1.04-26.0
Sandstone	36.4	10.4-98.8
Shale	88.4	88.4-400
Carbonate	10.4	1.04-15.6
Coastal suspended matter	nda	0.52-10.9
Deep-sea clay	93.6	57.2-109
Marine sediment	nda	10.4-36.4
River sediment	nda	0.00-104
River suspended sediment	187	nda
Sandy sediment	26.0	15.6-36.4
Fine-grained sediment	62.4	36.4-83.2
Clay	120	31.2-588
Soil	98.8	1.04-3020

Table 1.5.2.1 Chromium content of natural solids (from Richard *et al.*, 1991)
("nda" - no data available)

The octahedral ionic radius of Cr^{3+} is 0.615 Å and is between that of Al (0.53 Å) and Fe (0.645 Å). Therefore many Cr^{3+} compounds tend to be isostructural with the corresponding Al^{3+} and Fe^{3+} compounds, and Cr^{3+} ions often substitute for Al^{3+} , Fe^{3+} , Ti^{4+} (0.68 Å) and Mg^{2+} (0.72 Å), in octahedral cavities. Substitution for Al^{3+} is the most common, and layer aluminosilicates, which are common crustal components (e.g. muscovite, chlorite, montmorillonite, and illite), will commonly have lattice-bound Cr^{3+} (Burns and Burns, 1975).

About 70 % of Cr found in sediments is lithogenic in nature (Guptu and Chen, 1975; Chester *et al.*, 1976; Wagemann *et al.*, 1977), with a relatively minor fraction bound to hydrous oxide surfaces or held in ion exchange positions. This fraction of Cr may be more readily available for biological uptake and remobilization than lattice-bound Cr and may therefore form an important reservoir for exchangeable Cr at the sediment-water interface.

1.5.3 Toxicity and Anthropogenic Sources

Chromium is an essential nutrient for plant and animal metabolism (glucose metabolism, amino- and nucleic acid synthesis). However, when accumulated at high levels, it has been linked to nausea, skin irritation and mucus membrane disorders (Dulka and Risby, 1976). At concentrations of ~ 0.1 mg/g body weight, it can become lethal (Mertz, 1974; Ajmal *et al.*, 1984). Cr(VI) is the most toxic form for both plants and animals (Benoit, 1976; Mathur *et al.*, 1977; Ross *et al.*, 1981; Ajmal *et al.*, 1984).

Chromium is a commonly used industrial metal and is classified as a priority pollutant by various environmental agencies in the world. Steel manufacturers, electroplating operations and refineries frequently serve as anthropogenic sources of Cr. Other industrial compounds such as dyes, anti-fouling agents, primers, fungicides and wood preservatives cause Cr pollution problems in localized areas (Capuzzo and Anderson, 1973). The maximum accepted level in drinking water is 1 μM dissolved Cr (E.P.A. criteria, Kopp and Kroner, 1968; Commission of European Communities and the World Health Organization).

1.5.4 Redox Behavior

The distribution between Cr(III) and Cr(VI) is regulated by redox reactions. The redox speciation can be defined by the equilibrium (Elderfield, 1970):



The ratio of Cr(VI)/Cr(III) from the above equation is given by:

$$\log [\text{Cr}(\text{VI})/\text{Cr}(\text{III})] = 6\text{pH} + 3\text{p}\epsilon - 66.1$$

In oxygenated seawater, assuming a pH of 8.1 and a p ϵ of 12.5, Cr(VI) should predominate by a factor of $\sim 10^{20}$. If the p ϵ of seawater is controlled by the O₂/H₂O₂ couple, the p ϵ of seawater with [H₂O₂] = 0.1 μM would be 6.5 (Pettine and Millero, 1990). This would imply that Cr(VI) still predominates by a factor of ~ 100 . However, under reducing conditions, with a p ϵ value of -4 (controlled by the SO₄²⁻/H₂S couple) and average pH of 7.5, Cr(III) becomes the dominant species. The p ϵ -pH relationship for dissolved Cr species is shown in Figure 1.5.4.1.

Although thermodynamic equilibrium considerations show that Cr(VI) should be the dominant form of Cr under oxic conditions, the slow oxidation kinetics of Cr(III) must be taken into account. Because of the different coordination numbers between Cr(III) and Cr(VI), considerable rearrangement of the first coordination sphere must occur in the oxidation and reduction of Cr. This necessitates complex mechanisms for both reactions (Early and Cannon, 1965). Rearrangement of the Cr(III) coordination sphere is additionally limited by its kinetic stability which constitutes an additional constraint to the oxidation of this species (Taube, 1970).

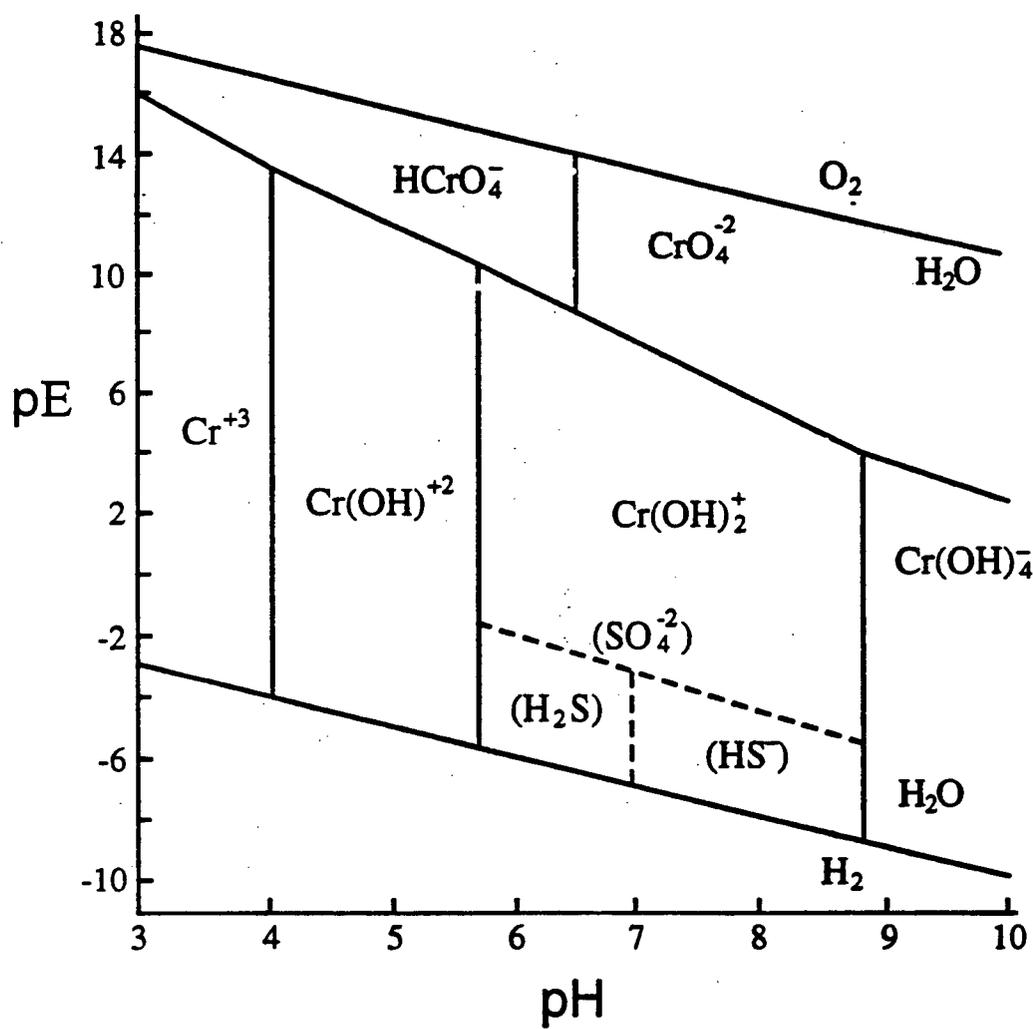


Figure 1.5.4.1 pE - pH relationship for aqueous Cr (from Cranston, 1979).

The most likely oxidants in natural systems capable of oxidizing Cr(III) to Cr(VI) include dissolved oxygen and manganese oxides. The oxidation of Cr(III) by dissolved oxygen has, however, been reported to be very slow. Schroeder and Lee (1975) obtained a pseudo-first-order rate constant of 0.37/yr for the oxidation reaction with O₂, but Eary and Rai (1987) did not observe any oxidation at 27 °C even after 24 hours. The oxidation of Cr(III) by manganese oxides is reported to be more rapid than by dissolved oxygen, but the reaction rates depend on the Mn oxides used. Second-order rate constants with respect to Mn oxide and Cr(III) ranging from 0.0008 M⁻¹ s⁻¹ for γ -MnOOH (Nakayama *et al.*, 1981c) to 1.34 M⁻¹ s⁻¹ for an unspecified oxide (Schroeder and Lee, 1975) have been observed. A more recent study has shown that H₂O₂ may also be a significant oxidizing agent in seawater with a half-life of 45 days (Pettine and Millero, 1991). The authors of this latter study suggest that a Cr-borate complex may be involved in the oxidation.

Cr(VI) is strongly oxidizing and reacts rapidly with numerous reducing agents found commonly in the environment. Eary and Rai (1988,1989) found that Cr(VI) is reduced in seconds to hours by ferrous ions and ferrous-ion containing oxide and silicate minerals. Reduction by organic matter (Schroeder and Lee, 1975; Bartlett and Kimble, 1976; James and Bartlett, 1983) and by H₂S(g) (Smillie *et al.*, 1981) have also been reported.

1.5.5 Organic Complexation and Photochemistry

Recent investigations into the chemical speciation of trace metals in seawater have indicated that copper, cadmium, nickel, cobalt and zinc occur complexed to various extent with dissolved organic material (Douglas *et al.*, 1986; Van den Berg, 1984; Buckley and Van den Berg, 1986; Bruland, 1989; Nimmo *et al.*, 1989; Zhang and Wollast, 1990; Moffett *et al.*, 1990; Moffett, 1995). Under certain environmental conditions, these organo-metal species constitute the predominant form of the metal and can therefore significantly contribute to the overall geochemistry of the metals.

Although Cr-organic matter interactions have been reported in the literature for some time, their impact on the overall aquatic geochemistry of this element are not well understood. Some of the earliest research on Cr-organic complexation was conducted in the Sea of Japan by Nakayama *et al.* (1981a). Organic chromium speciation was reported to contribute as much as 60 % of the total dissolved Cr. Organic chromium concentrations in the shelf waters off the eastern coast of Australia were found to range from 0.002 to 0.160 nM (Mackey, 1984). A similar study of Australian coastal waters north of Sydney revealed that 0-90 % of total dissolved Cr was organically bound (Ahern *et al.*, 1985).

Indirect photoreduction was reported by Kieber and Helz (1992) to be an important mechanism for the transfer of Cr to the particulate phase. A strong diel maximum in Cr(III)/Cr(VI) ratio (determined using the iron co-precipitation technique with analysis by GFAAS) during the early afternoon, coinciding with a maximum in H₂O₂ concentration was observed. This maximum coincided with the Fe(II) maximum produced from the photoreduction of Fe(III). Incubation experiments with both filtered and unfiltered seawater showed changes in Cr species only in unfiltered samples confirming that particles were required for indirect photoreduction of Cr(VI). In a proposed mechanism for the indirect photoreduction of Cr(VI), sunlight is absorbed by particles containing ferric oxyhydroxides (Kieber and Helz, 1992). This releases Fe(II) into solution and oxidizes organic matter which is sorbed to the particle surface. The Fe(II) then reacts in solution with CrO₄²⁻ to produce Cr(III) and colloidal Fe(OH)₃.

Kaczynski and Kieber (1994) have recently presented a detailed investigation on organic Cr speciation and its potential impact on Cr biogeochemistry using samples encompassing broad environmental areas. Levels of complexed Cr ranged from a few picomolar in open ocean organic-poor waters in the eastern South Atlantic to several nanomolar in inland DOM-rich waters. Organic Cr concentrations were positively correlated to both dissolved organic carbon and UV absorbance. Photolysis experiments indicated that the organic Cr species were easily photodegraded; in addition, laboratory inorganic Cr spike experiments showed rapid (~ 2 hr) complexation with dissolved organic matter.

1.5.6 Sorption Processes

Chromium(III) species, poorly soluble as mostly $\text{Cr}(\text{OH})_3^0$ and $\text{Cr}(\text{OH})_2^+$ are strongly attracted to the negative charge of deprotonated oxide surfaces (Cranston and Murray, 1980). Adsorption effects are therefore quite significant for cationic Cr(III). For instance, Benes and Steinne (1975) studied Cr(III) and Cr(VI) in river and lake waters and found that Cr(III) was associated with particles that could be centrifuged from the water, while the Cr(VI) could not be removed by particles. Using river and estuary water samples from the Columbia River, Cranston and Murray (1980) conducted spiking experiments with Cr(III) and determined that most of the Cr(III) spike was adsorbed by suspended particulate matter (SPM) in the 2-18 mg/L range within an hour. Similar results were reported by Mayer *et al.* (1983) using natural SPM levels (17 mg/L) from a Maine river with significant Cr(III) adsorption occurring in a few hours.

Adsorption is a relatively insignificant process for soluble Cr(VI) in oceanic systems where, at ambient pH, it is repelled by the deprotonated oxide surfaces. Thus chromate removal via sorption is not expected to be an important process; this anion is therefore highly mobile in aquatic systems.

1.5.7 Summary

In natural environments, the most stable oxidation states of Cr are Cr(III) and Cr(VI). Major Cr(III) dissolved species are Cr(OH)_2^+ and Cr(OH)_3^0 ; organic complexation also appears to be significant although the nature and extent are not well understood. The main forms of Cr(VI) in natural waters are soluble HCrO_4^- and CrO_4^{2-} . Cr(III) is thermodynamically unfavored in oxygenated waters, but once formed can persist due to its slow oxidation kinetics. Any oxidation or complexation reactions involving Cr(III) will be slowed by its kinetic stability. Cr(III) is strongly associated with the particle phase and only sparingly soluble, while Cr(VI) is highly soluble and has little affinity for the particle phase in most natural waters.

Chapter 2

MATERIALS AND METHODS

2.1 Instrumentation

2.1.1 Gas Chromatography

A Hewlett Packard 5890 series II gas chromatograph (GC) equipped with a 555.0 MBq ^{63}Ni electron capture detector was used in this study. The ECD-GC was run in the split mode with a split ratio of approximately 10:1. A J & W Scientific (Folsom, CA) DB 210 15 m x 0.25 mm o.d. capillary column with a 0.5- μm film thickness was used. The carrier gas, ultra high purity (UHP) grade hydrogen, was purified further by passing it through a molecular sieve trap and a hydrocarbon trap. The detector makeup gas, UHP grade nitrogen, was purified via a heated carrier gas trap and an indicating oxygen trap. Data handling from the GC runs was performed on an on-line Toshiba 3200 personal computer equipped with HP-Chemstation 3365 software. The GC conditions for the analysis of chromium in seawater as tris-(1,1,1-trifluoro-2,4-pentanediono)-chromium(III) ($\text{Cr}(\text{tfa})_3$) are summarized in Table 2.1.1.1

Injection port temperature	200 °C
Oven temperature	130 °C
Detector temperature	350 °C
Column head pressure	15 psi
Hydrogen carrier gas flow	2.6 mL/min
Nitrogen makeup gas flow	49 mL/min

Table 2.1.1.1 Gas chromatographic conditions for the analysis of chromium as tris-(1,1,1-trifluoro-2,4-pentanediono)-chromium(III)

2.1.2 Graphite Atomic Absorption Spectrometry

A Varian Spectra atomic absorption spectrometer (Varian Techtron Ltd., Mulgrave, Victoria, Australia), Model AA300/400, equipped with a Varian Techtron GTA-96 graphite-tube atomizer and Zeeman background correction was used for the determination of dissolved and particulate Mn and Fe as well as particulate Al. Sample solution were delivered to the furnace using a Varian Techtron PSC-56 programmable autosampler, controlled through an IBM (PS/2, Model 30) data station. Partition tubes coated with pyrolytic graphite were used for Mn and Al analysis and plateau tubes with pyrolytic graphite platforms were used for determination of dissolved and particulate Fe. Metal concentrations were calculated using the method of standards addition to correct for matrix effects, instrumental parameters suggested by the manufacturer were used with modifications where necessary.

2.2 Materials and Reagents

2.2.1 Water

Distilled deionized water (DDW) was obtained after distillation in a glass still (Barnstead/Thermolyne Corp., Dubuque, IA) and deionization through a "Milli-Q" deionization system (Millipore Waters Associates, Mississauga, Ont.). The output water had a resistivity of at least 18 M Ω cm.

2.2.2 Trace Metal Acids and Bases

Nitric, hydrochloric, hydrofluoric and acetic acids, prepared by double distilling at sub-boiling temperatures in quartz or Teflon[®] vessels (Seastar Chemicals, Sidney, B.C.), were used in all sample handling procedures where strict contamination control was necessary. Single sub-boiling quartz-distilled acids (Seastar Chemicals, Sidney, B.C.) and reagent grade acids (BDH Inc., Vancouver, B.C.) were used whenever ultra-low levels of trace metals in the acids were not required, such as plasticware cleaning. Ammonium hydroxide (Seastar) was used for digestion of

polycarbonate filters during the determination of suspended particulate metals in samples from Saanich inlet.

2.2.3 Chelating Ligand

The chelating ligand, 1,1,1-trifluoro-2,4-pentanedione (Htfa) (Aldrich Chemical Company, Milwaukee, Wisconsin) was purified by distillation (3-4 times) at atmospheric pressure in a Teflon[®] still constructed as described by Measures and Edmond (1986).

2.2.4 Solvent

Toluene (BDH, ACS or Omnisolve grades) was purified by distillation (2-3 times) through a 4 ft x 1.5 inch glass still. The distillate was monitored for extraneous peaks by injection into the gas chromatograph. Acetone (BDH, ACS grade) was used for rinsing the Teflon[®] reaction bottles and the separatory funnel during the extraction procedures.

2.2.5 Internal Standard

An internal standard, 2,6-dichlorobiphenyl (Chem. Service Inc., Westchester, PA) was used during Cr extractions and analysis by ECD-GC. It was spiked directly into the toluene at a concentration of approximately 100 ng/mL after the latter had been purified by distillation.

2.2.6 Trace Metal Standards

Certified atomic absorption (AA) standards (1000 ppm) for Cr, Mn, Fe and Al were bought from either Aldrich Chemical Company (Milwaukee, Wisconsin) or from Mallinckrodt (Paris, Kentucky) and used for calibration after dilution with DDW to appropriate concentration ranges.

2.2.7 Buffer

Quartz-double distilled acetic acid (Seastar Chemicals Inc., Sidney, B.C.) diluted with distilled deionized water (DDW) to give approximately 10% CH_3COOH and a 1 M NaAc/HAc buffer system, were used for pH adjustments. The 1M NaAc/HAc buffer was prepared from analytical grade sodium acetate (BDH) which had been purified by recrystallization two times. An alternate cleaning procedure for the sodium acetate involved treating the impure sodium acetate buffer solution in the same way as the seawater samples (described below) and using the redistilled Htfa ligand to scavenge any Cr present by liquid-liquid extraction. Both procedures were equally effective in producing NaAc which was clean enough for use in this study. The recrystallization procedure was chosen for all subsequent work as it was less time consuming.

2.2.8 Reducing Agent

Sodium sulfite solution (1 M) was used for the reduction of Cr(VI) to Cr(III). The impure salt (BDH ACS grade) was cleaned via extraction with the redistilled Htfa. This was done by adjusting the pH of the solution to approximately 6 with double distilled acetic acid (HAc) followed by solvent extraction with toluene in a similar manner to the seawater samples (described below). The solution was rinsed several times with the redistilled toluene to ensure that all the Htfa had been removed.

2.3 Methods

2.3.1 Seawater Collection

Seawater samples from the various locations for this study were all collected using trace metal clean techniques. In general, sample collection was accomplished by the use of either Teflon[®]-lined GO-Flo or modified Niskin bottles (General Oceanics, Miami, FL) suspended on either a clean hydrowire or Kevlar[®] line; bottle closure was effected with Teflon[®] messengers.

2.3.2 Plasticware Cleaning

Factory manufactured plasticware is normally not "trace metal clean" and requires further cleaning to leach out metals embedded on the surface during the manufacturing process. The materials cleaned were seawater bottles, pipette tips, GFAAS autosampler cups and other miscellaneous containers. They were made of either high density polyethylene (HDPE), low density polyethylene (LDPE) or Teflon[®] depending on resistivity to acids and solvents and desired blank levels after cleaning. The cleaning procedure involved an initial double rinse of the containers with 5-10 mLs of acetone to remove grease and organic contaminants. This was followed by two rinses with DDW after which the containers were soaked with 4 N reagent grade HCl either for 3 days at 60 °C or for one and a half weeks at room temperature. They were then rinsed again twice with DDW and stored for at least a week (or until needed) with 1-2 % quartz-double distilled HNO₃.

2.3.4 pH

pH measurements were performed using an Orion SA 520 pH meter equipped with a Model 91-02 general purpose combination electrode.

2.3.5 Shaking

Shaking of the Cr samples during the solvent extraction procedure was accomplished with a Burrell Model 75 wrist action shaker.

2.3.6 Solvent Extraction

Cr(III) reactions are generally quite slow and heating of the samples in a microwave oven (Samsung Model MW257OUC) was used to speed up the Cr(III)-tfa chelation reaction (details in section 2.3.9). A low volume make-shift Teflon[®] separatory funnel for the extractions was constructed as described by Measures and Edmond (1989).

2.3.7 Microwave Digestion

To quantitatively extract Mn, Fe and Al from the suspended particulate materials collected during filtration of samples, microwave assisted digestion of the filters was used (see section 2.3.10 for digestion procedure). This was accomplished with the use of a Model MDS-205 microwave oven (CEM Corp., Matthews, NC), with a maximum rated power of 600 W. The oven was equipped with a CEM pressure transducer for monitoring the internal pressure of one of the digestion vessels. Sequential stages of varying power and time intervals were programmable.

2.3.8 Processing and Handling of Cr Samples

Whenever shipboard determinations were not possible, it was necessary to preserve the sample in a manner that would not appreciably alter the Cr speciation. A quick freeze method consisting of an acetone/dry ice mixture which froze the samples in under 5 minutes was used; frozen samples were then stored in a freezer until analysis. Seawater samples for Cr determinations were generally not filtered as Cr determinations at sea on filtered (0.40 μm Nuclepore) and unfiltered samples gave essentially the same results. This is probably because these samples were not acidified prior to analysis as in most other methods and as a consequence Cr leaching from suspended particles was negligible.

Chromium species determinations were performed at sea immediately after sample collection or in the laboratory using samples that had previously been either stored frozen or stored acidified at low pH. Seawater samples which had been stored frozen were allowed to thaw out on the bench for about 1 hr and Cr(III) and total Cr were then determined on them as

described below. In stored acidified samples, all Cr(VI) is reduced to Cr(III) within 24 hrs (Campbell and Yeats, 1981) and only the total dissolved Cr could be determined in the samples.

2.3.9 Chromium Determinations by ECD-GC

Most Cr speciation techniques rely on operational separations of Cr(VI) and Cr(III) based on their differing chemical properties. The analytical method used for the determination of Cr species in this dissertation employed electron-capture detection of the volatile trifluoroacetylacetone derivative of Cr(III) formed via solvent extraction with toluene (Mugo, 1991; Mugo and Orians, 1993). Total labile Cr was determined as Cr(III) after reduction, with Cr(VI) obtained by difference. During analysis of seawater samples from a reducing environment where Cr(III) is expected to dominate, it was discovered that a fraction of Cr in these samples was not being detected by the analytical scheme as initially developed. Modifications to the original ECD-GC technique to allow measurement of this "non-labile" Cr were implemented (details below). The different Cr species determined are dependent on the sample pretreatment step. These operationally defined fractions are explained below.

2.3.9.1 Labile Chromium(III)

Seawater samples (15 mLs) for the determination of Cr(III) were measured into 60 mL Teflon[®] reaction bottles using an adjustable 10 mL Eppendorf pipette. The pH was adjusted from that of seawater (7.5-8.3) to the extraction value of 6.0 (\pm 0.2) with the addition of 20 μ L 10% Q-CH₃COOH. The purified Htfa ligand (100 μ L) was then added, followed by the addition of 1 mL of the internal standard-spiked toluene. The bottles were shaken manually for five seconds to ensure mixing of the reagents; they were then heated in the microwave oven, four at a time, for 3 min at 20 % power level. To reduce pressure build-up inside the bottles during microwave heating, bottles were partially deflated by squeezing the walls in prior to capping, allowing room for expansion. The bottles were removed from the microwave and shaken for five

seconds and then returned for another 3 min at the same power level. At the end of this period the sample temperature was 65-70 °C.

During cooling, samples were shaken for 10 min on the mechanical wrist action shaker, fully cooled to room temperature, then carefully transferred to the Teflon[®] make-shift separatory funnel where the aqueous layer was separated and discarded. The organic layer was shaken for 10 s with 1 mL of DDW to help prevent the formation of emulsions from Ca and Mg hydroxides which can occur when NaOH is added in the next step. The layers were allowed to separate and the organic layer then shaken for 20 s with 1 mL of 1 M NaOH. This washing step with base was critical as it served to destroy the excess ligand which would oversaturate the detector if not removed. After separation, the organic layer was rinsed twice with a 1 mL of DDW to remove traces of the NaOH. The extract was then transferred to a clean glass vial with a Teflon[®]-lined cap (once chelate formation was complete and the excess ligand removed, the organic extracts are virtually immune from any Cr contamination; contact with glassware is therefore not a problem at this stage). The extracted sample was ready for injection into the GC at this stage or it could be stored at room conditions for 1-2 days. For long term storage, the extracts were stored in the freezer at -15 °C and were stable for several weeks. The fraction of Cr measured in this sample is considered to be the "free" inorganic Cr(III) in solution excluding organic and/or colloidal forms that may be present (see Chapter 6). It is referred to in the thesis as "labile Cr(III)".

2.3.9.2 Total Labile Chromium

The reaction between the ligand, 1,1,1-trifluoro-2,4-pentanedione, and chromium is specific for Cr(III); for total dissolved Cr determination it was necessary to convert Cr(VI) to the reduced state before chelation could occur. For previously frozen (and unacidified) samples, 20 µL of the 10% CH₃COOH and 200 µL of the 1 M sodium sulfite reducing agent were added to 15 mLs of thawed sample to achieve optimum extraction conditions. In samples which had been stored acidified at pH 2, Cr(VI) was reduced within 24 hrs and thus no reducing agent was added. These samples were brought to the extraction pH by the addition of 2 mLs (for each 15 mLs of

sample) of the 1M NaAc/HAc buffer. In both cases the samples were then treated in a similar manner as described for labile Cr(III) determinations above. The Cr measured in these samples is referred to as "total labile Cr". Cr(VI) is obtained by the difference between "total labile" Cr and "labile Cr(III)" determined above.

2.3.9.3 Total Oxidizable Chromium

To determine the fraction of bound Cr in samples from reducing environments (presumably bound in colloidal and/or organic forms), modifications were made to the ECD-GC procedure in a similar manner as described by Cutter (1982) and Ahern *et al.* (1985). To a third 15 mL seawater sample acidified to pH 2.3 with 6 N Q-HCl (Seastar Chemicals, Sidney, B.C.), 200 μ L of 30 % hydrogen peroxide solution was added and the sample heated in the microwave oven for a total of 5 min with regular shaking and release of pressure. The sample bottle was then stirred with a Teflon[®] coated magnetic stirrer while being irradiated with UV light from a 275 W lamp for 1 hr. At the end of the period, sample was allowed to cool, the sodium sulfite reducing agent added, and the pH raised to 6.0 ± 0.2 with NaAc/HAc buffer. Chromium was then extracted and analyzed as described above. The Cr concentration in this sample is referred to as "total oxidizable Cr". The difference between "total oxidizable Cr" and the "total labile Cr" constitutes an estimate of the bound Cr fraction referred to as the "non-labile" Cr fraction.

2.3.10 Processing and Analysis for Manganese, Iron and Aluminum

Seawater samples for dissolved and particulate Mn and Fe as well as particulate Al were filtered in a laminar flow hood equipped with a HEPA filter in the shore-based laboratory 4-8 hrs after collection. Filtration (0.4 μ m Nuclepore) at 15 psi pressure was achieved using a Millipore[®] pump hooked up to the side-arm of a HDPE filtration flask. Care was taken to minimize contact with air during filtration. The filters containing the suspended materials were dried in the laminar flow hood and kept in ziplock bags which were stored in the freezer. The filtrate was acidified to pH \sim 2 with 6 N Q-HCl and stored until analysis. Samples were diluted (10-500 fold) with

acidified DDW either on the bench or through instrumental pre-programming and delivered to the furnace using a Varian Techtron PSC-56 programmable autosampler. Standards additions were used to correct for matrix effects during analysis by GFAAS.

Digestion of the filters for determination of suspended metal concentrations was done in small (approximately 4 mL) thick-walled Teflon[®] digestion vials. The first step in the digestion process involved the addition of 1 mL of Q-NH₄OH solution to the vials followed by heating the vials for two hours on a hot-plate inside the flow hood. At the end of this period, the ammonia solution had digested the polycarbonate filters leaving a brown residue at the bottom of the vials. Half a milliliter each of Q-HCl, HNO₃ and HF was then added to the vials which were tightly capped. They were then transferred to Teflon[®] bombs in the microwave digestion oven for 45 min at 40 % power level. The digests were evaporated slowly to dryness on the hot plate for approximately 6-8 hrs after which 250 µL of Q-HNO₃ was added and again taken to dryness on the hot plate. The digests were then redissolved in a total of 4 mL 2 N Q-HNO₃; this final solution was analyzed for particulate Mn, Fe and Al by GFAAS again using standards addition for matrix correction.

Chapter 3

Chromium Distribution in Open Ocean and Coastal Environments

3.1 INTRODUCTION

Knowledge of the distribution of elements in seawater, particularly for those elements present in more than one oxidation state, is useful in the understanding of general geochemical processes. Our understanding of trace element oceanic distributions has significantly expanded over the last two decades due to advances in sampling protocols and analytical methodology. Progress in trace metal geochemistry has continued to be the subject of excellent periodic reviews (Burton and Statham, 1982; Bruland, 1983; Whitfield and Turner, 1987; Donat and Bruland, 1995). Trace element distributions are influenced by a combination of source and removal functions as well as physical transport and biochemical transformations; studies therefore continue in an effort to identify which particular processes control the geochemistry of any given element.

Chromium exists in nature in two main oxidation states, Cr(III) and Cr(VI), which are characterized by very different chemical properties and geochemical behaviors. Thermodynamic calculations (Elderfield, 1970) predict that in oxygenated waters, the dominant Cr species is chromate as the stable, soluble tetrahedral oxyanion, CrO_4^{2-} . Cr(III) exists as the unstable hydrolyzed species, $\text{Cr}(\text{OH})_3^0$ or $\text{Cr}(\text{OH})_2^+$ which bind strongly to particles and organic material (Osaki *et al.*, 1983; Douglas *et al.*, 1986) and are predicted to dominate in anoxic environments. Literature data on Cr species distributions in marine environments are scarce and variable, which may be due in part to differences in analytical speciation techniques used by various investigators; it may also result from the kinetic stability of Cr(III).

Open ocean environments provide an opportunity to assess global geochemical controls on trace element distributions. These controls may be more apparent or magnified in nearshore environments; moreover, coastal environments are generally more accessible and therefore amenable to more thorough sampling. Thus a study combining both open ocean and nearshore sampling locations offers the greatest potential for understanding the processes responsible for the marine geochemistry of a given trace element. This is particularly the case for redox sensitive

elements whose distributions can be influenced by redox and scavenging processes at ocean boundaries, with the effects transported offshore.

In an effort to further our understanding of Cr geochemical processes, chromium species were measured at two stations in the eastern North Pacific and in several British Columbia inlets. Total dissolved Cr was also analyzed in stored samples (filtered and acidified) from the central North Atlantic, near Bermuda. These results will be used to assess the factors responsible for the distribution in both oceanic basins and to identify coastal and nearshore effects on the distributions.

3.2 MATERIALS AND METHODS

3.2.1 Sample Collection and Analysis

Seawater samples for this study were collected during three different cruises, using trace-metal clean sampling procedures. Vertical profiles from the eastern North Pacific were collected at station P26 (50°00'N, 145°00'W) and station P20 (49°34'N, 138°40'W) aboard the C.S.S Endeavour in October, 1991. Chromium measurements in three B.C. inlets were undertaken during the Department of Oceanography, University of British Columbia, programme of study of British Columbia inlets in August, 1993. Samples were collected on board the C.S.S Vector from station KN 7 in Knight inlet (50°48'N, 125° 37'W, 519 m), station DE 10 in Dean inlet (52°50'N, 126°60'W, 165 m) and station JV3 in Jervis inlet (49°48'N, 124° 02'W, 678 m).

Seawater samples during these two cruises were collected using either 10 or 30 L Teflon[®]-lined, acid washed, GO-Flo bottles (General Oceanics, Miami, FL) mounted on Kevlar[®] line and triggered with Teflon[®] messengers. Chromium subsamples were drawn from the GO-Flo bottles directly into acid-washed LDPE or Teflon[®] bottles using an acid-cleaned Teflon[®] tube with care being taken at all times to minimize any possible contamination. The samples were then transferred to a portable high efficiency pure air (HEPA) unit (Canadian Cabinets, Mississauga, Ont.) in the shipboard laboratory for analysis of chromium.

Shipboard determinations of Cr in filtered (0.4 µm Nuclepore) and unfiltered seawater samples showed no difference, probably because the samples were not acidified to the usual low pH values (1-2) common in other analytical procedures, and therefore possible leaching of Cr from particles was negligible. The samples were therefore not filtered which allowed more rapid analysis and minimized possible contamination inherent in the filtration procedure. Data for temperature and salinity were taken from a CTD probe. Dissolved oxygen measurements using the Winkler titration method were performed onboard by Hugh Mclean of the Department of Oceanography, UBC. Results for nutrients were obtained from the Institute of Ocean Sciences (IOS), Sydney, B.C.

Seawater samples from the central North Atlantic, near Bermuda, were collected using modified 5 L Niskin bottles (General Oceanics) mounted on a stainless steel hydrowire, by E. A. Boyle and colleagues from the Massachusetts Institute of Technology (MIT). The samples were filtered through 0.4 μm Nuclepore filters then acidified to $\text{pH } 2 \pm 0.1$ and stored in acid leached polyethylene bottles. Under these conditions all the Cr is reduced to Cr(III) within 24 hr (Campbell and Yeats, 1981), and only total labile Cr can be determined. All sample handling and processing was done in a laminar flow bench in the shore-based laboratory.

Chromium determinations in the seawater samples were accomplished by using the electron capture detector gas chromatographic (ECD-GC) technique (Mugo and Orians, 1993). Labile Cr(III) reacts with 1, 1, 1-trifluoro-2,4-pentanedione (Htfa) to form the $\text{Cr}(\text{tfa})_3$ complex which is extracted into 1 mL of toluene. Total labile Cr is extracted in a similar manner after sodium sulfite reduction of Cr(VI) to labile Cr(III), with Cr(VI) obtained by difference. In stored acidified samples, all Cr is in the Cr(III) form and a reducing agent is not necessary. Aliquots of the extracts (1 μL) are analyzed directly by ECD-GC with concentrations determined by calibration standards processed by the same procedure. An internal standard, 2,6-dichlobiphenyl was used during extractions and analysis. The detection limits at sea are 0.06 nM for labile Cr(III) and 0.26 nM for total labile Cr. The precision (1s) is $\pm 5 \%$ at 0.65 nM labile Cr(III) and $\pm 3 \%$ at 4.70 nM total labile Cr.

3.3 RESULTS

3.3.1 Chromium Distributions in the Pacific and Atlantic

3.3.1.1 Eastern North Pacific Stations

Nutrient and Cr species data for Station P26 are shown in Figure 3.3.1. Only a partial vertical profile was collected at station P20 (Figure 3.3.2) and thus the results from station P26 will be used as representative data from the eastern North Pacific.

The concentration of labile Cr(III) is low at both stations P26 and P20 (0.03-0.29 nM) in comparison to Cr(VI). Labile Cr(III) values at P26 are lowest near the surface with higher values at 1000 m. Higher labile Cr(III) concentrations are also seen at this station in the bottom waters, reaching 0.21 and 0.29 at 3000 and 4000 m, respectively. In general, labile Cr(III) values at station P20, which is located closer to the shore, are somewhat higher than at P26. Higher labile Cr(III) concentrations at this station occur in the surface waters and also at intermediate depths with a high value of 0.17 nM at 1500.

Since labile Cr(III) on average accounts for less than 5 % of total labile Cr at both stations, Cr(VI) and total labile Cr distributions are fairly similar. Cr(VI) concentrations range from 2.2 to 4.1 nM whereas total labile Cr values range from 2.4 to 4.3 nM. The most obvious feature in the distribution is the subsurface maximum for both Cr(VI) and total labile Cr at both stations. A surface depletion of ~ 20 % results in a relative maxima centered at 400 m with total labile Cr values of 4.2 nM and 3.4 nM at P26 and P20, respectively. Total Cr and Cr(VI) then decrease and are invariant in intermediate waters. A slight increase is observed towards the sediment-water interface at P26.

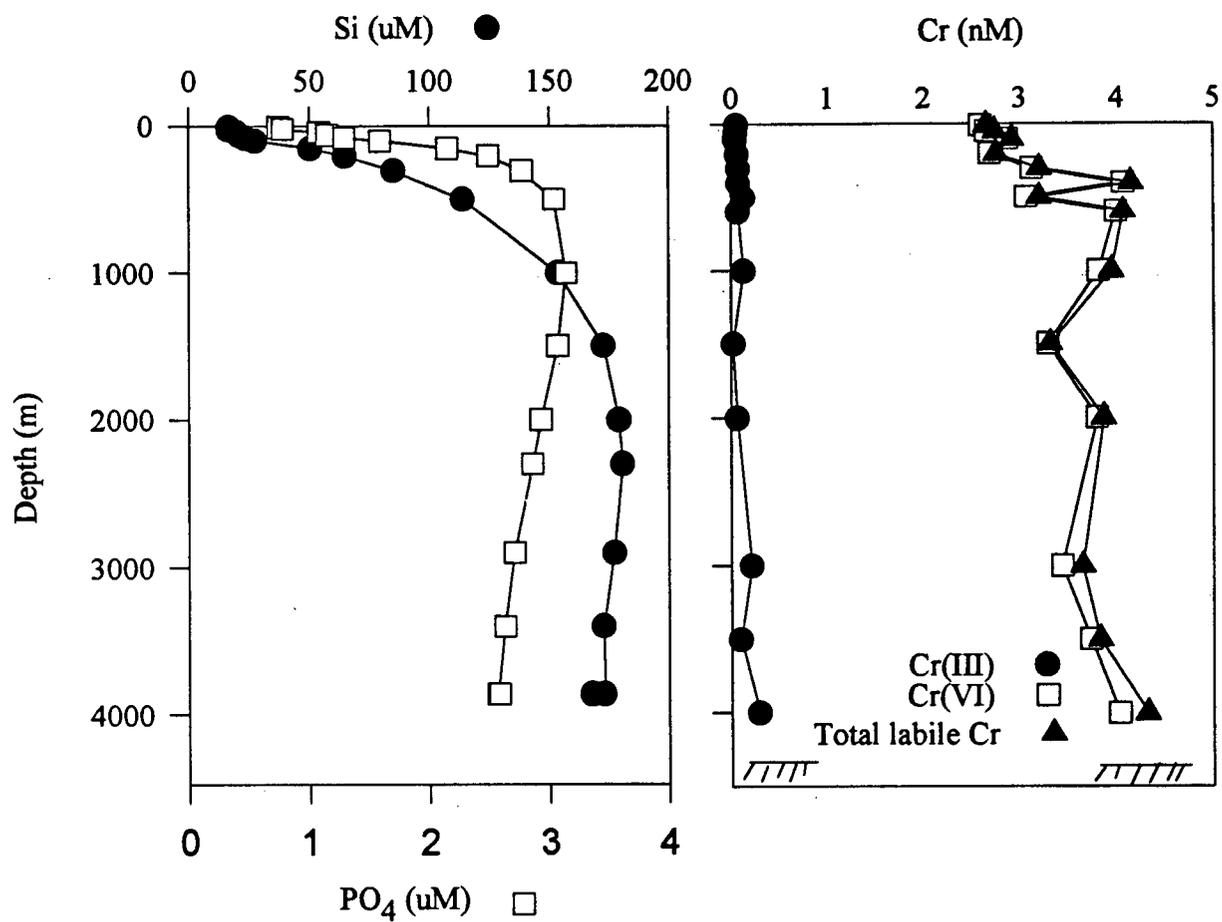


Figure 3.3.1 Nutrient and Cr data for Station P26 in the eastern North Pacific

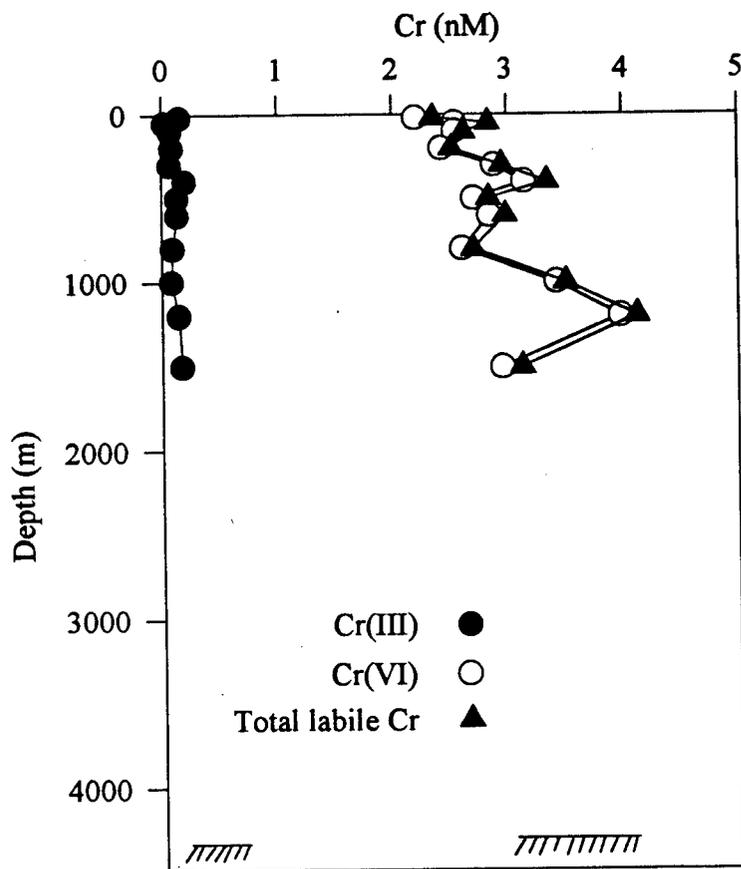


Figure 3.3.2 Cr species at Station P20 in the eastern North Pacific

3.3.1.2 North Atlantic

Distribution of total dissolved Cr and nutrients at the central north Atlantic station near Bermuda (BDA) are shown in Figure 3.3.3 (Cr species determinations were not possible in these acidified samples). Total dissolved Cr values range from 2.9 nM at the surface to 3.9 nM at 3000 m. Like the Cr profiles from the Pacific ocean, a surface depletion of ~ 20 % is evident with a total labile Cr subsurface maximum at 300 m (3.8 nM). The intermediate water column total labile Cr values remain approximately constant at 3.0 nM with a slight increase in bottom waters.

3.3.1.3 Comparison With Other Results

Not many data sets are available in the literature on oceanic Cr concentrations. The Atlantic results compare well with those of Jeandel and Minster (1987) in the North Atlantic and Campbell and Yeats (1981) in the Labrador Sea and the northwest Atlantic. Dissolved Cr concentrations in the Pacific are better documented than those in the Atlantic. Reported labile Cr(III) values, however, tend to be variable; low labile Cr(III) values with slightly higher levels in intermediate waters were reported in the northeast Pacific (Murray *et al.*, 1983; Cranston, 1983; Jeandel and Minster, 1987) whereas labile Cr(III) values in the northwest Pacific were reported to be below the detection limit by Measures (personal communication, 1991). In general, Cr results from the Atlantic and Pacific oceans in this study are in good agreement with data from other investigators.

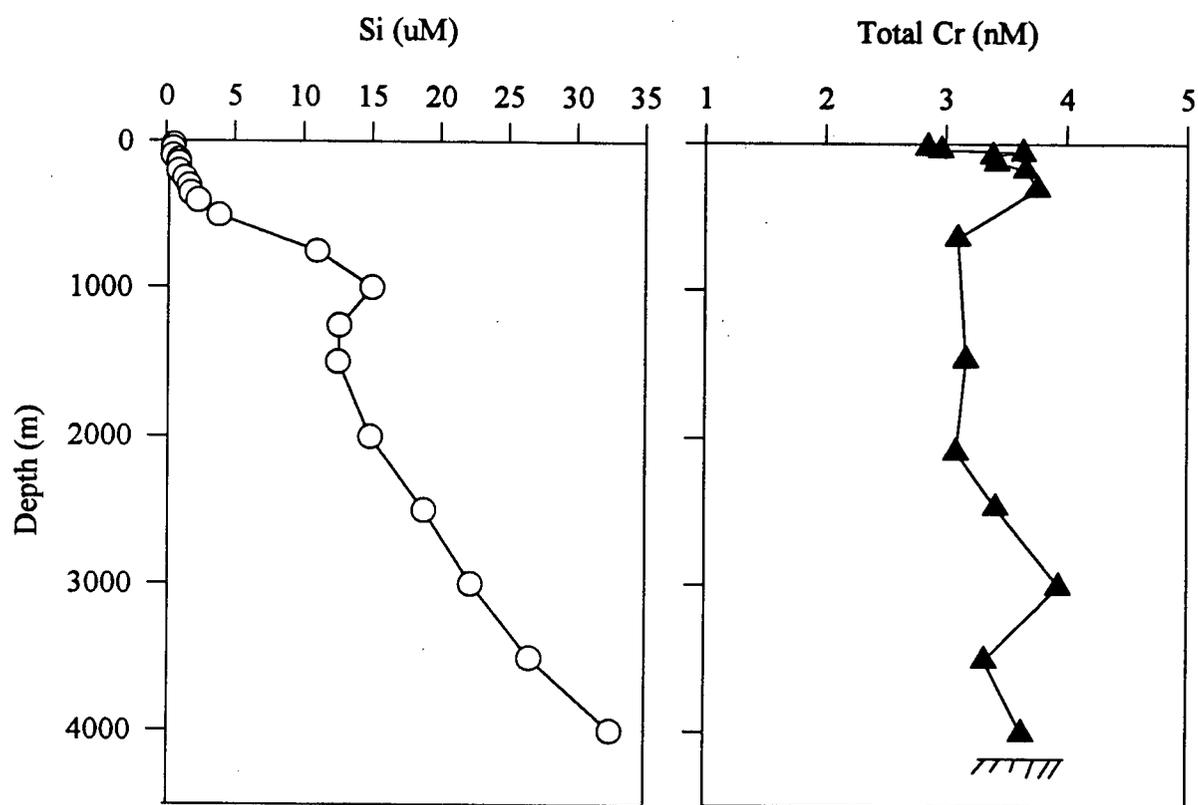


Figure 3.3.3 Silicate and total Cr data for BDA Station in the central North Atlantic

3.3.2 Chromium Species in British Columbia Inlets

3.3.2.1 Knight Inlet

Data for station KN 7 in Knight inlet are presented in Figure 3.3.4. The labile Cr(III) values range from 0.35 to 0.77 nM whereas total labile Cr ranges from 3.4 nM to 4.7 nM. Labile Cr(III) and total labile Cr concentrations are on average higher than those found in the open ocean Pacific stations (P20 and P26) with labile Cr(III) making up roughly 16 % of the total dissolved Cr. Higher labile Cr(III) values (0.65-0.77 nM) were found near the surface than in the deeper waters. Total Cr and Cr(VI) distributions show a surface depletion (~ 25 %) relative to values in intermediate waters. Towards the bottom, an increase in Cr concentration is observed, with the deeper waters having total labile Cr concentrations of 4.4 and 4.5 nM at 400 m and 450 m, respectively.

3.3.2.2 Dean Inlet

Cr species, hydrographic and dissolved oxygen data for station DE 10 in Dean Inlet are presented in Figure 3.3.5. Total Cr values range from 3.9 to 4.5 nM and show a similar distribution to Cr(VI) (concentrations 3.2-4.1 nM). A small subsurface maximum for Cr(VI) and total labile Cr is seen in the upper water column at 30 m. Labile Cr(III) concentrations (0.40-1.0 nM) are higher than average oceanic (Pacific) values with surface values being highest. On average, labile Cr(III) makes up 12 % of total labile Cr.

3.3.2.3 Jervis Inlet

Cr species distributions at station JV3 in Jervis inlet (Fig 3.3.6) show similar features to the other two inlets. Labile Cr(III) values range from 0.43 to 0.75 nM (approximately 15 % of total labile Cr) with higher values near the surface relative to values at depth. Total Cr concentrations (3.3 to 4.7 nM) display a subsurface maximum at 50-100 m, decreases at mid-depth, then increases towards the bottom.

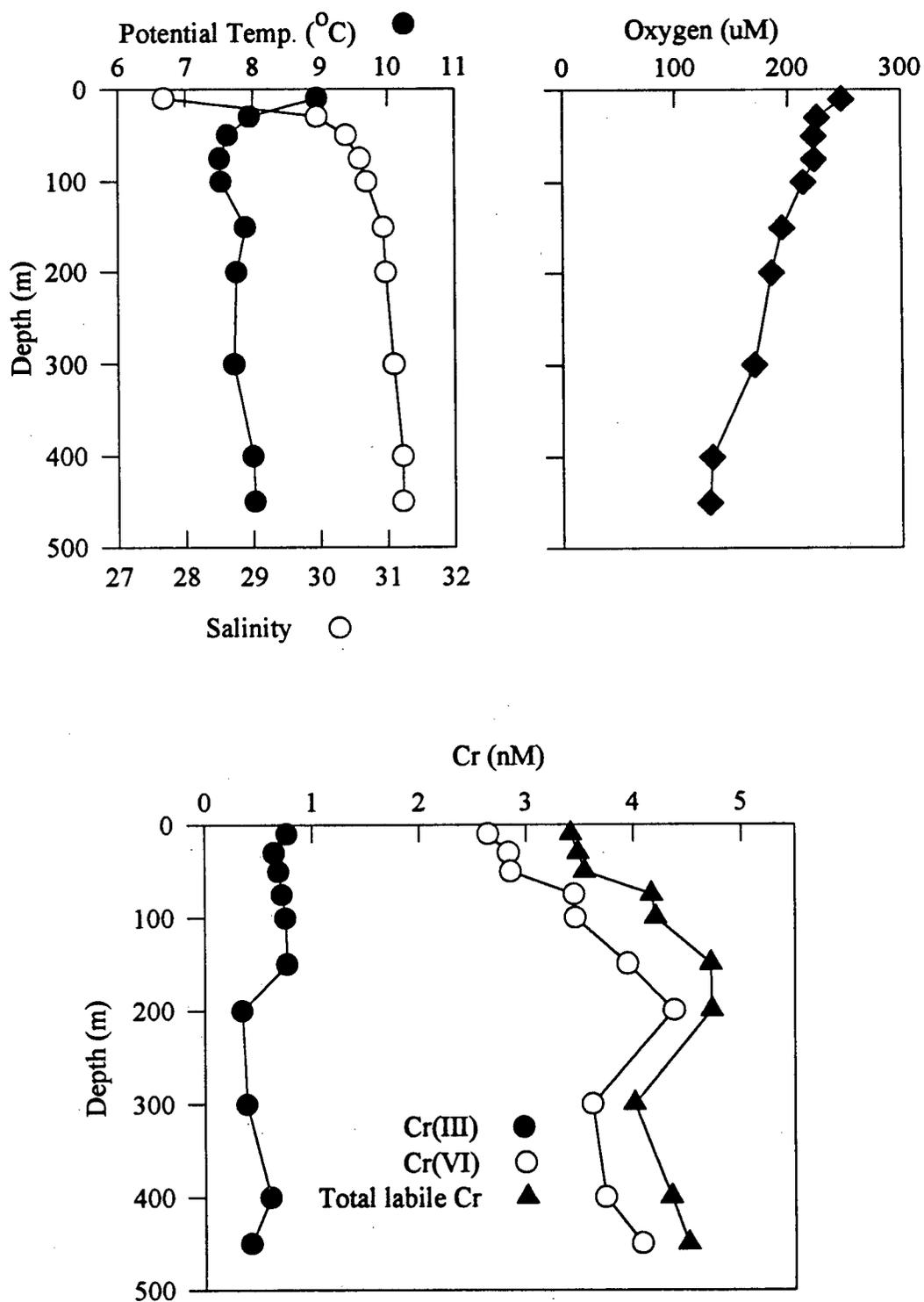


Figure 3.3.4 Hydrographic, oxygen and Cr data for Station KN7 in Knight Inlet

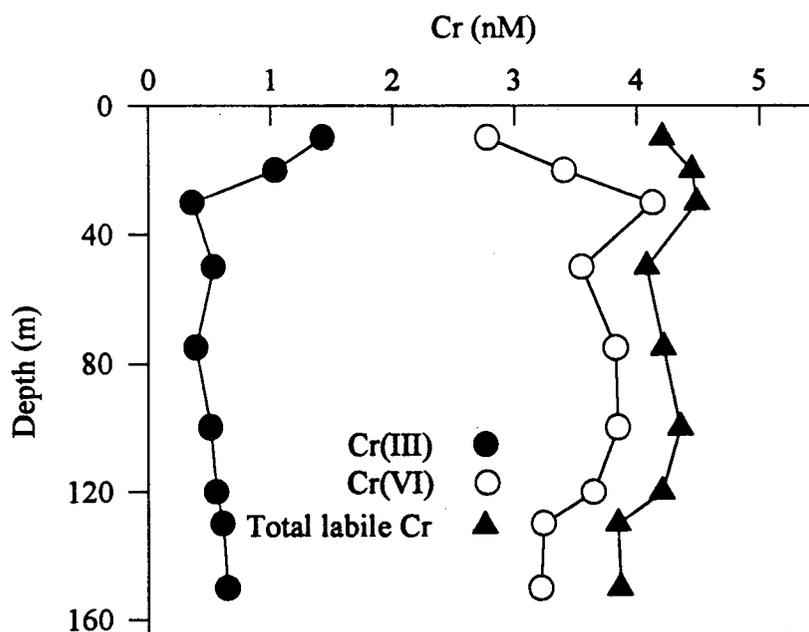
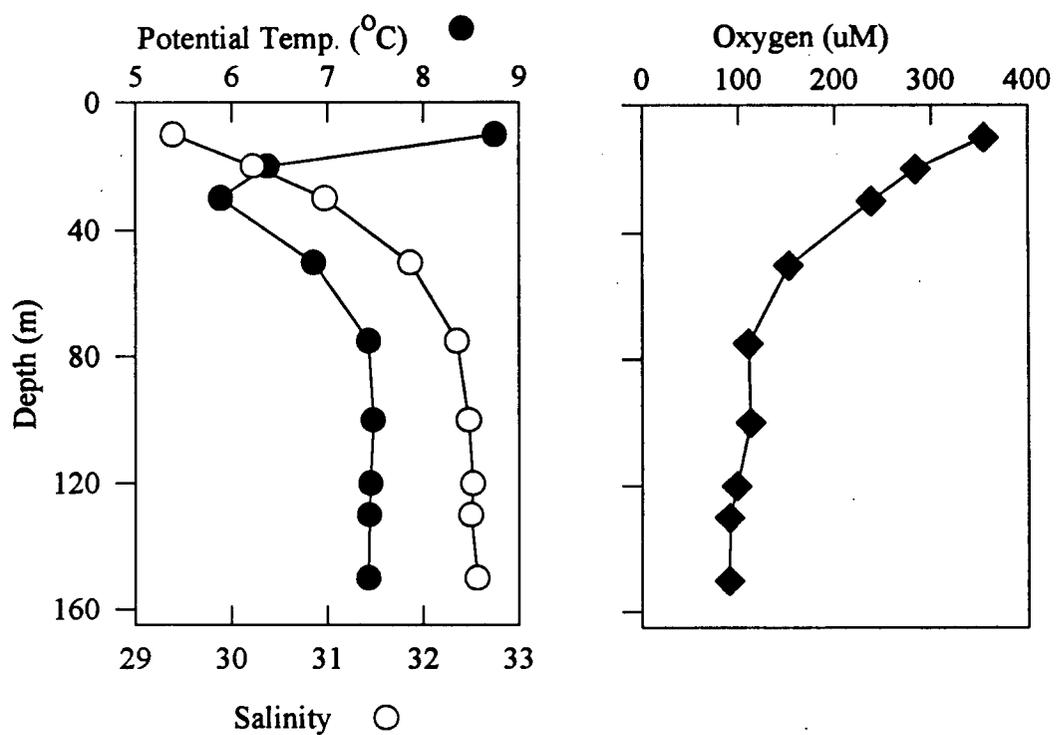


Figure 3.3.5 Hydrographic, oxygen and Cr data for Station DE10 in Dean Inlet

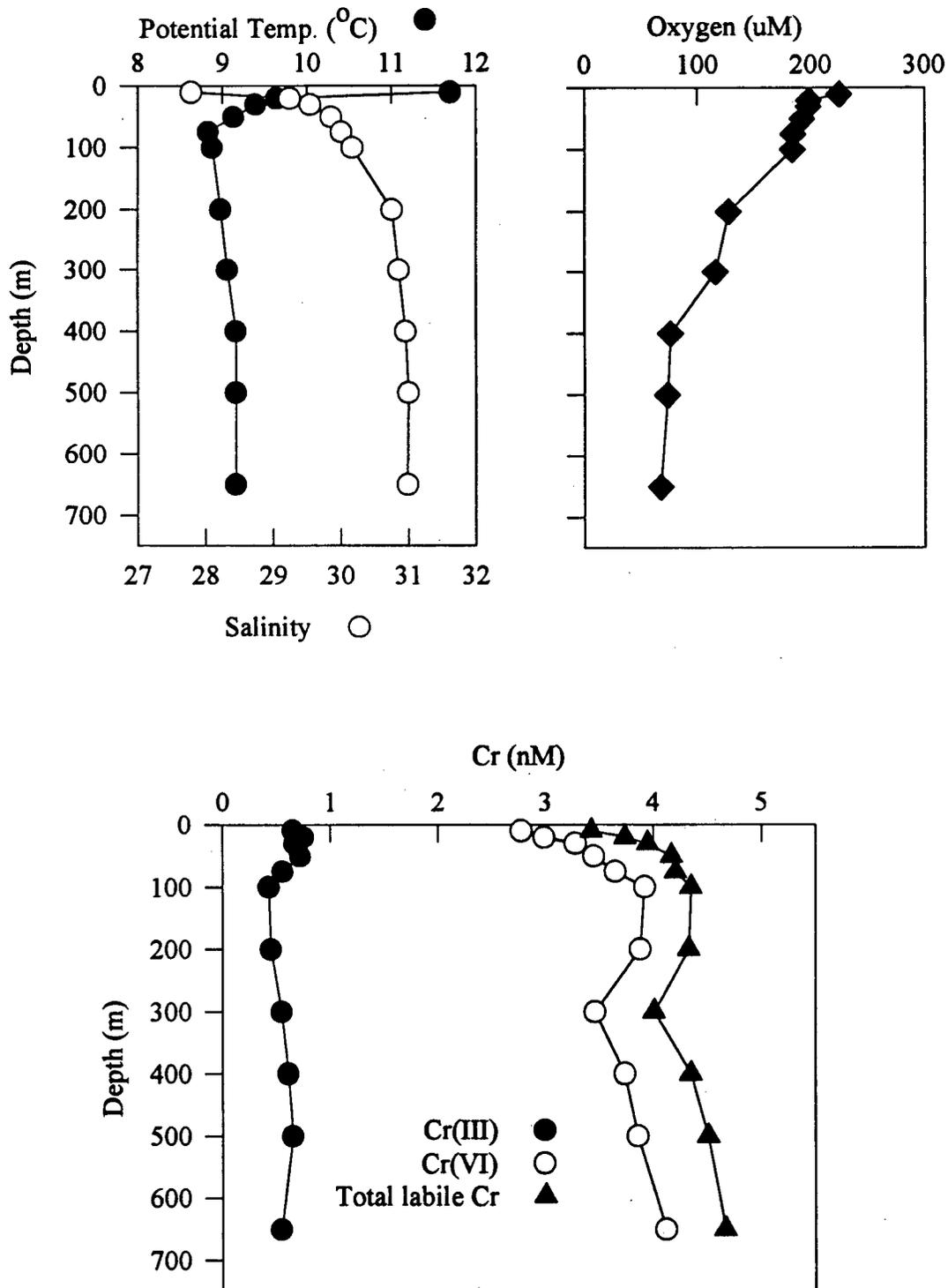


Figure 3.3.6 Hydrographic, oxygen and Cr data for Station JV3 in Jervis Inlet

3.3.2.4 Summary of Cr Results in B.C. Inlets

The striking feature of Cr distributions in the three B.C. inlets is the higher labile Cr(III) values compared to the open ocean Pacific results. Labile Cr(III) concentrations average 0.60 nM in the inlets which is 4-6 times higher than at stations P20 and P26. Labile Cr(III) makes up between 12 and 16 % of the total dissolved Cr in the inlets compared to an average of < 5 % in the open ocean stations. Total Cr values are also, on average, higher: 4.2 nM compared to 3.7 nM in the open ocean Atlantic and Pacific stations. The similarity between chromium species distributions in the inlets suggests that similar geochemical factors may be influencing distributions in all three locations. These results support earlier findings of higher Cr values in Nootka Sound, B.C. compared to the open ocean (Mugo, 1991; Mugo and Oriens, 1993). They are also in agreement with Cr results from Jervis Inlet by Cranston (1979) who found Cr(III) values ranging from 0.2 to 1.6 nM, and with other data from nearshore and inland areas. Murray *et al.* (1983) in their study of Cr and Mn geochemistry in the Eastern Tropical Pacific observed higher Cr values near the continental margin. Elevated Cr(III) values were also found in the upper 100 m of Cascadia basin and towards the continental shelf by Cranston (1983), as well as in a variety of coastal and inland natural waters in Southeastern US (Kaczynski and Kieber, 1993).

3.4 DISCUSSION

Three main features of chromium distributions can be identified from the results in this study: lower total labile Cr values at the surface relative to intermediate waters, a slight increase near the bottom, and higher labile Cr(III) and total labile Cr values in coastal areas compared to open ocean stations. The factors responsible for the distributions will be assessed in terms of physical and biogeochemical controls at the surface and possible scavenging and remobilization in intermediate and bottom waters. The open ocean profiles will be compared with results from B.C. inlets to assess likely coastal and nearshore controls.

3.4.1 Inter-basin Distribution Comparison

Chromium has been described as having a nutrient-type oceanic distribution (Campbell and Yeats, 1981; Cranston, 1983). Nutrient-type elements (e.g. Zn, Cd) like the major nutrients nitrate, phosphate and silica, are removed from the surface and remineralized into intermediate and deep waters as part of the major biogeochemical cycles associated with plankton productivity. They exhibit surface water depletion and have concentrations in the relatively young waters of the deep North Atlantic which are substantially less than those observed in the older North Pacific deep waters.

Vertical profiles of Cr at station P26 in the Pacific and at BDA station in the Atlantic both display similar features (Figures 3.3.1 and 3.3.3). The subsurface maxima are located between 50 and 400 m with total labile Cr values in intermediate waters more or less invariant with depth; concentrations then increase in bottom waters between 2000 and 4000 m. The deep waters of the Atlantic, however, have approximately the same total labile Cr values as the deep Pacific waters (3.48 nM vs. 3.85 nM average for bottom samples). This lack of an inter-ocean gradient suggests that Cr is not a true nutrient-type element.

3.4.2 Biological Incorporation

Of the two common Cr oxidation states, Cr(VI) is soluble, highly mobile and toxic to organisms. Cr(III) on the other hand is quite insoluble, thermodynamically unstable in oxygenated environments and is considered essential for the maintenance of glucose, lipid and protein metabolism (Langard and Norseth, 1979). Biological incorporation of Cr would be expected to proceed mainly via the uptake of the soluble and mobile chromate. Both intracellular and extracellular uptake mechanisms for Cr(VI) have been proposed (see Kieber and Helz, 1992 and references therein). Intracellular reduction of Cr(VI) results in Cr(III) trapped inside cells as the transport of this species through cell membranes is much less efficient than transport of Cr(VI) (Nieboer and Jusys, 1988). A plausible hypothesis for extracellular biological reduction postulates production of redox-labile organic extracellular products (e.g. catalase) by phytoplankton which can reduce Cr(VI) to Cr(III) when exposed to light (Kieber and Helz, 1992). The main drawback to this hypothesis is that both the identity and concentration of the postulated extracellular reductants are not known.

3.4.3 Association With Nutrients

Trace elements involved in the biological cycle of uptake and release show close association with the major nutrients in both oceanic basins. Elements which are associated with the more labile nutrients, nitrate and phosphate, show maximum concentrations near 1000 m (e.g. Cd). Other elements such as Zn and Ge have distributions that correlate directly with silica and have a deeper maximum near 2500 m. These latter elements are taken up, actively or passively, by organisms and incorporated into the opal skeleton. The uptake, regeneration and recycling processes which control silica distributions therefore also control their distributions.

It has been suggested that the Cr was associated with silica, and also possibly, phosphate in the oceans (Campbell and Yeats, 1981; Cranston and Murray, 1978; Cranston, 1983). Total Cr versus silica and phosphate data at station P26 in the central North Pacific are shown in Figure 3.4.1(a). A significant correlation ($r^2 = 0.85$) between the two, corresponding to a $\Delta\text{Cr}/\Delta\text{Si}$ ratio of 0.0079 nM Cr/ μM Si is seen. A ratio of 0.0076 nM Cr/ μM Si was reported by Cranston (1983) in the Cascadia Basin whereas Jeandel and Minster (1987) found $\Delta\text{Cr}/\Delta\text{Si}$ ratios of between 0.001 and 0.003 at various North Pacific stations. These results, of course, do not prove a direct relationship between Cr and biogenic silica; they can, however, be used to assess Cr association with biogenic hard-part cycles. Assuming that Cr is mainly incorporated into siliceous parts of organisms, the above ratio compares favorably with the chromium content of diatom skeletons, which, when leached to avoid contribution from coatings show a Cr/Si molar ratio of 0.0045 nM Cr/ μM Si (Kastner, 1981).

The correlation of total labile Cr with PO_4 at station P26 (Figure 3.4.1(b)) is not as good ($r^2 = 0.44$) as with silica; the correlation improves somewhat ($r^2 = 0.61$) if only samples between surface and 1000 m are considered (Figure 3.4.1(c)). These results therefore agree with previous findings that Cr may be involved in the biological cycle of uptake and remineralization with hard parts. However, Cr data from the central North Atlantic station (BDA) does not show a significant correlation with silica (Figure 3.4.2) which makes it impossible to do similar calculations. By comparing the distribution of silica in both basins (Figs. 3.3.1 and 3.3.3), the

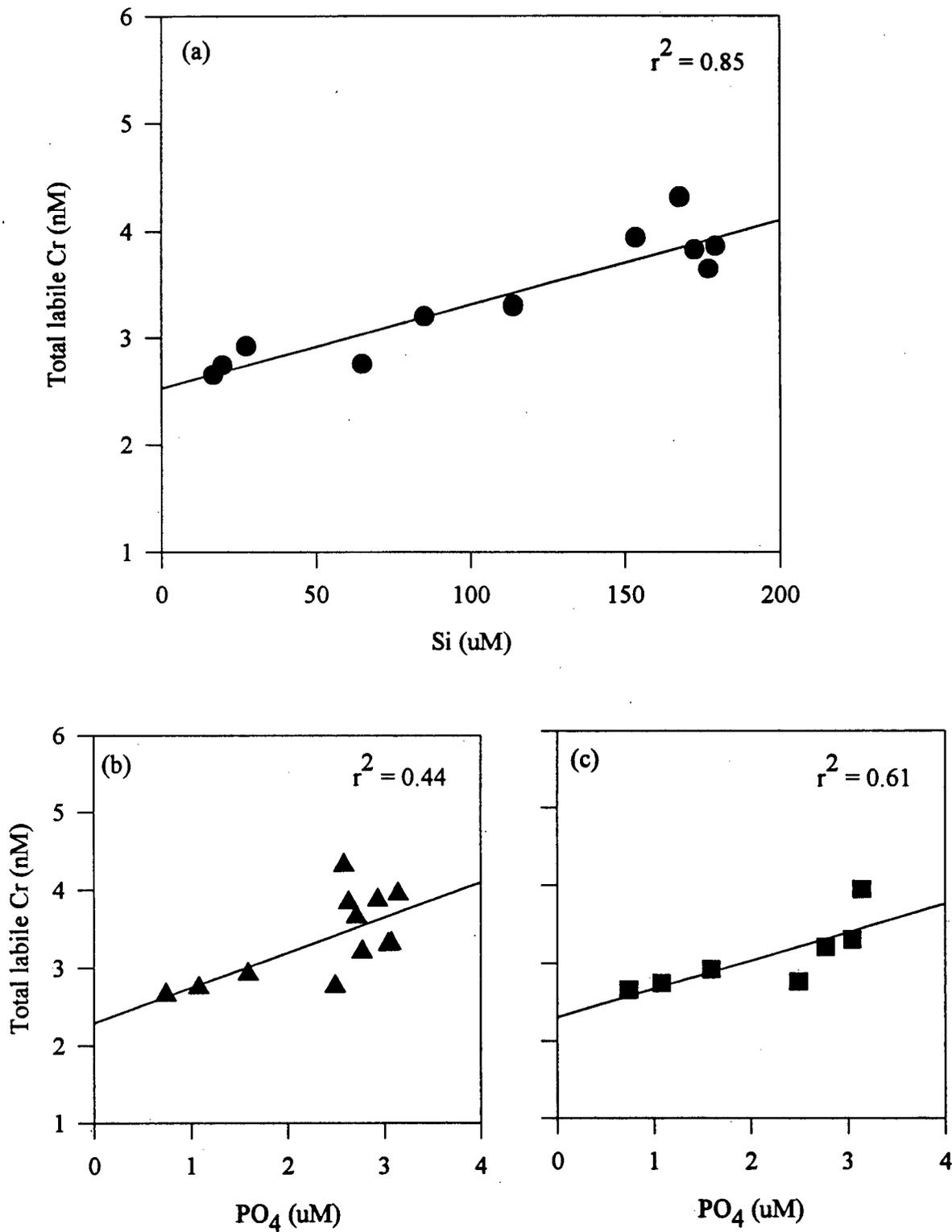


Figure 3.4.1: Total labile Cr at Station P26 plotted versus (a) Si (b) PO₄ (10-4000 m) and (c) PO₄ (10-1000 m)

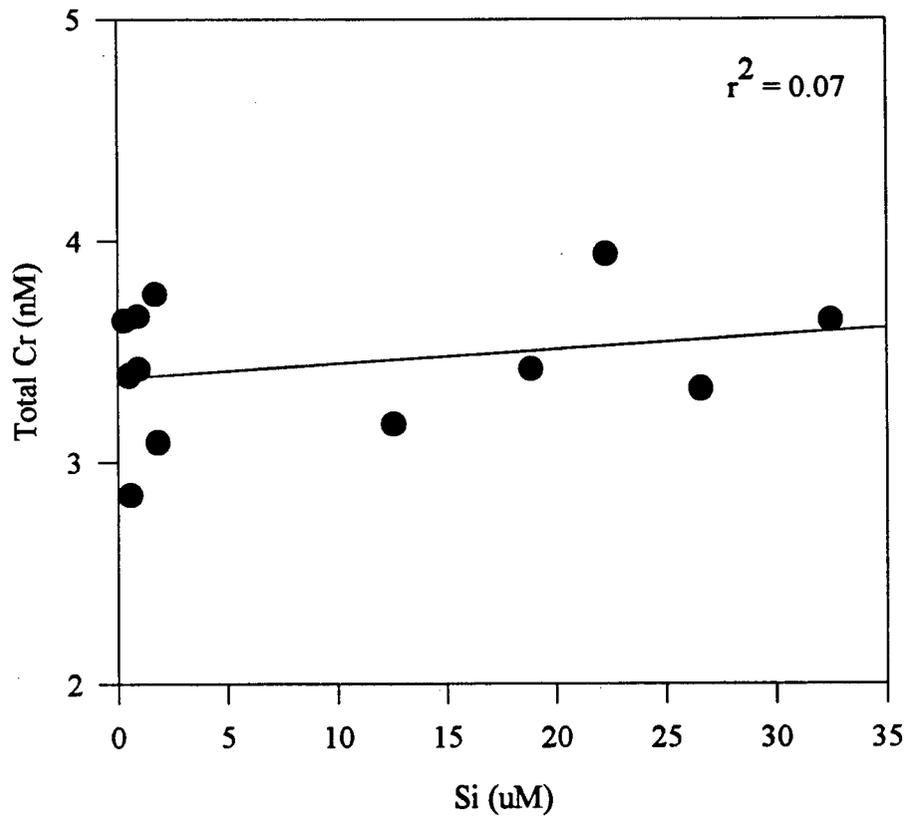


Figure 3.4.2 Total Cr versus Si data at BDA Station in the central North Atlantic

enrichment in the deep Pacific relative to the deep Atlantic is apparent. The deep water total labile Cr values in the two oceanic basins, however, do not show a similar fractionation.

Cr results from the NW Mediterranean (van den Berg *et al.*, 1994) display features similar to those seen in both the Atlantic and the Pacific but with no apparent Cr-nutrient correlations. Surface enrichment (~ 40 %) in total Cr from the central Mediterranean relative to similar nutrient-depleted Atlantic surface waters (Sargasso Sea) was attributed to sources within the Mediterranean Basin itself (Sherrell and Boyle, 1988).

Chromium profiles in the northwest Atlantic Ocean (Campbell and Yeats, 1981) and in the Cascadia Basin off the coast of Washington (Cranston, 1983) all show slight surface depletion and slightly higher values in the bottom waters. Campbell and Yeats (1981) report a positive correlation with silica and a less significant correlation with phosphate. Using multiple linear regression analysis, Cranston (1983) suggests that the equation relating total Cr to both silica and phosphate provides a better fit than a simpler equation using only Cr and silica. From this, he suggests that a portion of Cr is likely regenerated in shallow water and thus accounts for the subsurface Cr maximum. Similar conclusions can be drawn from the eastern North Pacific data but not from the central North Atlantic results.

In summary, it appears that Cr may be involved to some extent with the biochemical cycle in the oceans. The absence of interocean differences argues against Cr as a nutrient-type element and suggests that other processes e.g., photoredox and scavenging may be important in the distribution.

3.4.4 Photoredox Processes and Organic Matter Interactions

An alternate mechanism for control of Cr surface concentrations is via Cr photoredox processes. Photochemically induced redox reactions in seawater are not uncommon and can maintain disequilibria between redox couples. For instance, studies of manganese redox cycles in the oceans (Sunda *et al.*, 1983; Sunda and Huntsman, 1994; Waite *et al.*, 1988) have shown that photochemically induced reduction of manganese oxides may be responsible for maintaining the

pronounced surface water dissolved Mn maximum and a corresponding particulate Mn(IV) minimum. Various field studies also show that a significant steady-state concentration of Fe(II) can be maintained in surface sea water most likely via photochemically induced reduction of Fe(III), primarily as colloidal and particulate oxyhydroxides. For instance, Wells and Mayer (1991) demonstrated that sunlight exposure of iron hydroxides and oxides in seawater results in a large increase in the kinetic lability of iron and a subsequent increase in the bioavailability of the element.

Since Cr is a redox sensitive element like Mn and Fe, it is possible that its geochemistry in surface waters may too be influenced by photoredox processes. In-situ Cr(VI) reduction by photolytically generated Fe^{2+} was shown to be an important estuarine process (Kieber and Helz, 1992). This process involves the absorption of light by iron-organic colloidal matter which results in the production of Fe^{2+} , which in turn rapidly reduces Cr(VI) to Cr(III). Cr(III) thus formed can undergo dispersal in the water column via physical mixing processes or be sorbed onto suspended particles and removed from the water column when the particles sink. Depending on the intensity of physical mixing processes via advection and diffusion and the water column stratification, the photoredox processes may maintain Cr disequilibria in surface waters and also, possibly, deeper in the water column. Photochemically induced reduction of Mn(IV) to Mn(II) was recently shown to occur through the mediation of humic acids with the rate being dependent on various factors including organic loading (Spokes and Liss, 1995). It is possible, therefore, that the 4-6 times higher labile Cr(III) values in nearshore areas might result from increased photoreduction of Cr(VI) due to higher Fe and/or DOM. Higher Cr(III) values (up to 1.38 nM) were also reported in the coastal waters of Brittany, France by Jeandel and Minster (1984). Cranston (1983) found higher Cr(III) values in the upper 100 m in vertical profiles from Cascadia Basin, off the coast of British Columbia and Washington.

Another important factor which may impact Cr geochemistry particularly in coastal areas is direct Cr interaction with dissolved organic matter (DOM). Recent investigations into the chemical speciation of trace metals in seawater using electroanalytical techniques have shown that

copper, cadmium, nickel, cobalt and zinc occur complexed to various extent with dissolved organic material (Douglas *et al.*, 1986; van den Berg, 1984; Buckley and van den Berg, 1986; Bruland, 1989; Nimmo *et al.*, 1989; Zhang and Wollast, 1990, Moffett *et al.*, 1990; Moffett, 1995; Donat and van den Berg, 1992). Under certain environmental conditions, these organo-metal species constitute the predominant form of the metal and can therefore significantly contribute to the overall geochemistry of the metals. Direct Cr interaction with organic matter can be via reduction of Cr(VI) by DOM constituents, e.g., fulvic acids (Eckert *et al.*, 1990) or through DOM-Cr(III) complexation (e.g., Nakayama *et al.*, 1981a; Kaczynski and Kieber, 1994).

Higher dissolved organochromium complexes were reported in coastal and inland DOM-rich waters relative to open ocean organic-poor waters (Kaczynski and Kieber, 1994). These complexes were also shown to be easily photodegradable resulting in release of inorganic Cr(III) even after short time exposure to ambient sunlight; Cr-organic matter complexation was also rapid with the majority of the metal bound within 2 hrs. Coupled with physical advective and diffusive mixing processes, and the well known kinetic stability of Cr(III) species, organic matter-Cr interaction is therefore one way in which concentrations of Cr(III) that exceed thermodynamic predictions can be maintained, particularly in nearshore and surface waters.

Photoreduction of Cr(VI) with subsequent removal of Cr(III) via sorption is therefore a possible mechanism through which Cr depletion in surface waters of both open ocean and coastal environments can be maintained. Cr-organic matter interactions either via reduction of Cr(VI) and/or through the formation of organochromium species can maintain higher levels of Cr(III) in higher DOM coastal environments relative to open ocean areas. It is not possible at the moment to distinguish between biological uptake or photoredox and Cr-DOM interactions as the more important process in controlling Cr distributions in surface waters. In coastal areas, both processes may be important, whereas in oligotrophic waters, effects of photoredox processes may dominate.

3.4.5 Horizontal Transport From Ocean Boundaries

Various trace element distributions can be affected by ocean boundaries through scavenging or redox reactions at the boundaries with subsequent transport along isopycnal surfaces (Bacon *et al.*, 1976; Landing and Bruland, 1980). Average labile Cr(III) values are higher (0.11 nM) at station P20 which is located closer to the shore than at station P26 (0.08 nM). As well, labile Cr(III) and total labile Cr concentrations in the nearshore stations in B.C. inlets are also higher than the open ocean stations. Cr values in Cascadia Basin (Cranston, 1983) showed increase towards the continental margin. Thus it is impossible to rule out horizontal effects but it is difficult to use this source to explain the location of the subsurface maxima in the 50-400 m depth range.

3.4.6 Processes Affecting Deep Water Concentrations

A common feature in Cr oceanic distributions is the increase near the sediment-water interface. This suggests possible Cr remobilization either at the interface or within the sediments followed by diffusion into the overlying waters. The water column behavior of an element which shows increasing concentrations with depth may be determined by plotting the concentration of the element versus a conservative tracer such as salinity or potential temperature (Craig, 1974). Distributions which increase linearly display conservative behavior, a convex distribution indicates net release and a concave distribution indicates net removal (Figure 3.4.6.1). These relationships hold in locations of linear salinity-potential temperature plots denoting horizontal advection influences are minimal.

The salinity-potential temperature plot for the deep waters at station P26 in the eastern North Pacific (Figure 3.4.6.2 (a)) is linear below 1500 m which reflects the process of vertical advection of bottom water and diffusive mixing with the overlying intermediate waters. A plot of total labile Cr versus salinity for depths below 1500 m at station P26 (Fig 3.4.6.2(b)) show a concave deviation pattern from the conservative line which suggests that in addition to a simple two-endmember mixing, scavenging removal affects Cr in the water column. The salinity-potential temperature plot for data from BDA station (Figure 3.4.6.3(a)) is not as good as at P26 suggesting that horizontal effects may be a factor. In addition, the salinity-total labile Cr plot (Figure 3.4.6.3(b)) does not display a clear trend in the data and therefore no attempt will be made to model the central North Atlantic results.

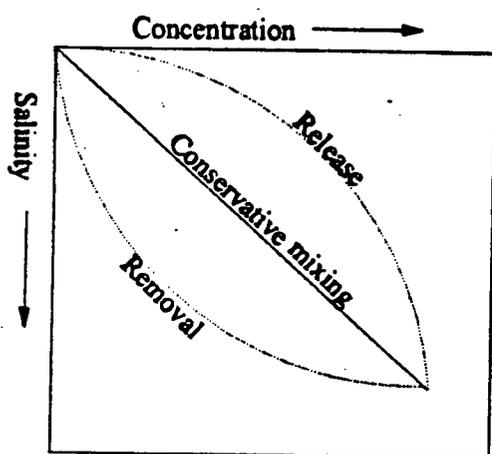


Figure 3.4.6.1 The elemental concentration versus salinity plots in deep waters showing the distributions obtained for conservative behavior, elemental release and removal by particle scavenging.

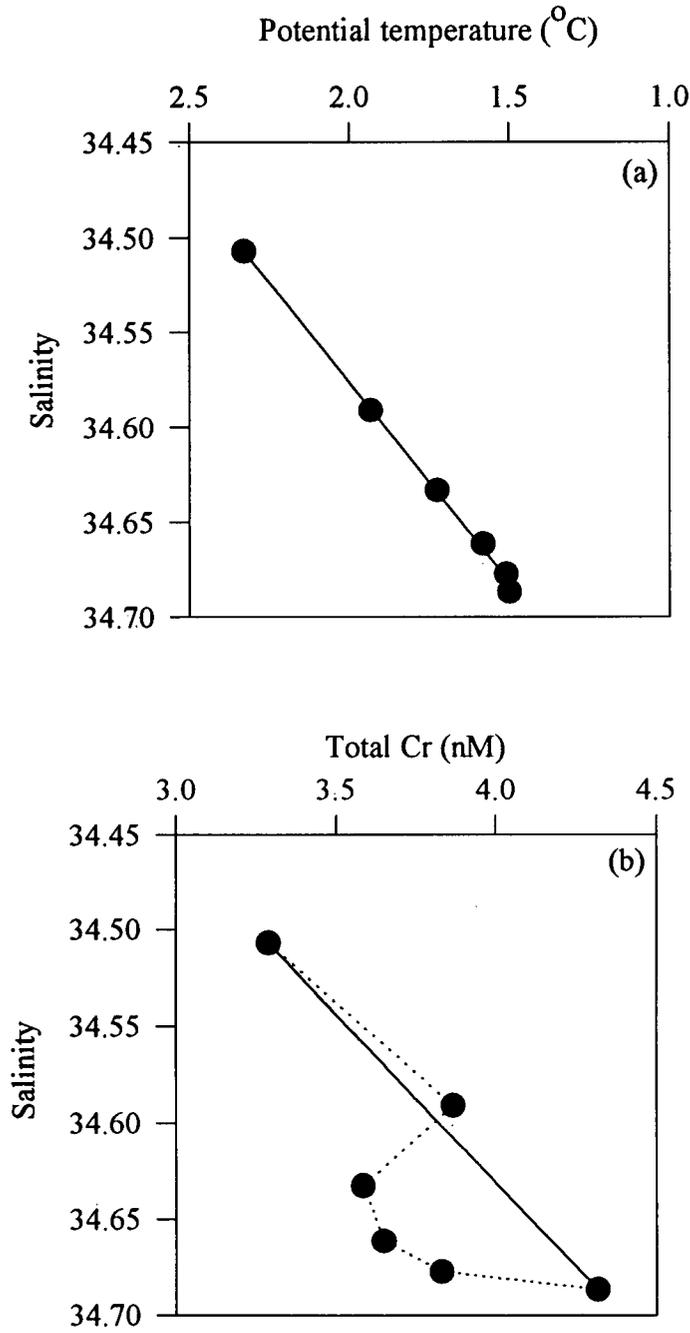


Figure 3.4.6.2 (a) Salinity-potential temperature and (b) Total Cr-salinity relationships for Station P26

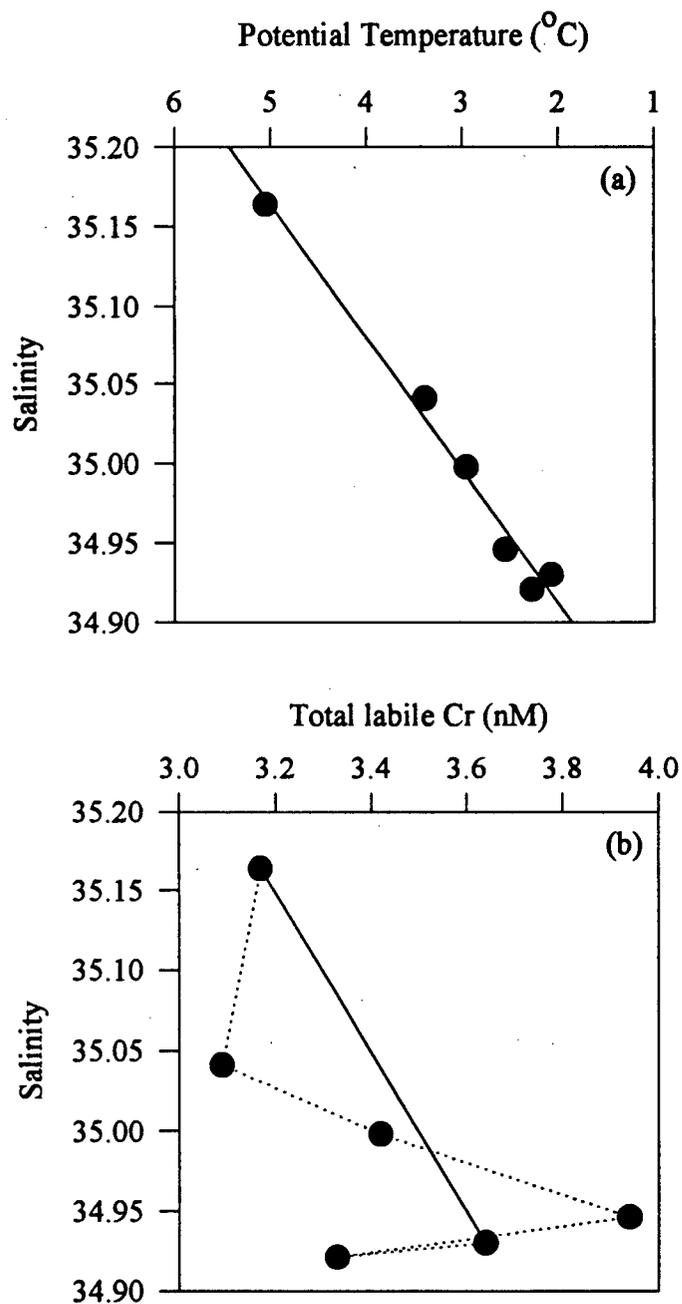


Figure 3.4.6.3 (a) Salinity-Potential temperature relationship and
(b) Total labile Cr plotted as a function of salinity for BDA station

Assuming steady state conditions, the water column processes can be modeled using a one-dimensional vertical advection-diffusion model as conceived by Craig (1974) and demonstrated for Cu by Boyle *et al.* (1977). The model can be expressed as:

$$0 = K (\partial^2[C]/\partial z^2) - W (\partial[C]/\partial z) + J \quad \text{equation 1}$$

where K is the vertical eddy diffusivity, W is the vertical advection velocity (positive downwards), [C] is the concentration of the element under consideration, z is the depth and J is the term that accounts for scavenging removal. The solution to this equation can be rearranged (Boyle *et al.*, 1977) as:

$$[C] = \alpha + (J/W) z + \beta S \quad \text{equation 2}$$

where α and β are constants and S is the salinity. From equation 2, J/W, α and β can be determined from multiple linear regression of [C] vs. S and z. The value of J, the scavenging term, can be determined assuming an upwelling rate (W) of 3.5 m/yr as estimated using radioisotopes (Craig, 1974). The scavenging residence time (as a "half-life") is calculated from the following equation:

$$\tau_{1/2} = \ln 2 / \{W(J/W) / [C]_{ave}\} \quad \text{equation 3}$$

The vertical-advection-diffusion model results for station P26 are shown in Table 3.4.6.1. It is important to stress that these results are subject to errors in the estimation of J/W and also errors arising from the small scale of vertical total labile Cr variation. A scavenging residence time for total labile Cr at station P26 of 2200 yrs obtained. A shorter residence time (1200 yrs) is calculated if the total labile Cr value (3.87 nM) at 2000 m which lies above the conservative mixing line is not taken into account in the calculation. The scavenging residence times obtained are longer than the 740 years estimated in the oxygen minimum zone of the East Pacific Rise

(Murray *et al.*, 1983). The shorter residence time in the East Pacific Rise likely results from more intense reductive scavenging of Cr(VI) in this low oxygen environment.

Parameter	Results ^a	Results ^b
α (nM)	33.90	125.9
β (nM)	-0.898	-3.580
J/W (nM/yr/m)	0.00035	0.00063
W(m/yr)	3.500	3.500
deep [total labile Cr] _{avg} (nM)	3.850	3.820
$t_{1/2}$ (yr)	2200	1200

Table 3.4.6.1 Results for the vertical-advection diffusion model for total labile Cr in the deep waters of the eastern north Pacific (P26). ^aall data, ^bwithout the total labile Cr value (3.87 nM) at 2000 m.

The increase in concentration in the bottom waters despite scavenging suggests that Cr remobilization is taking place in the sediments. The flux (F_B) can be crudely estimated using the method of Munk (1966) as:

$$F_B = -W[C]_B + K (\partial C / \partial z)_B \quad \text{equation 4}$$

where W is the vertical advective velocity, K is the vertical eddy diffusion coefficient, [C] is the Cr concentration, z is the depth. The subscript B refers to the change of concentration with depth at the seafloor. Using an estimate of $3.2 \times 10^7 \text{ cm}^2 \text{ yr}^{-1}$ for K (Gargett, 1984), the flux needed to support bottom and deep water distribution of total labile Cr at station P26 is $5120 \text{ nM Cr m}^{-2} \text{ yr}^{-1}$.

3.4.7 Possible Scavenging and Remobilization Processes

Due to the particle reactive nature of Cr(III) and the non-reactive nature of CrO_4^{-2} , the most likely removal mechanism for Cr is via reductive scavenging. Reduction can be as a result of biological uptake and/or photoredox processes in surface waters in both open ocean and coastal areas. Reductive scavenging can be expected to be more pronounced in low oxygen regions such as seasonally suboxic and anoxic basins and oxygen minimum zones. Annual Cr(VI) removal and increase of colloidal/organic Cr is evident during the stratified summer months in Saanich inlet (Chapter 4); total labile Cr also decreases to a minimum at the oxic-suboxic interface of the Black Sea (Chapter 5). In the East Pacific Rise, Murray *et al.* (1983) found that total Cr decreases sharply to a minimum at the top of the oxygen minimum. Similar observations have been made in the suboxic zone of the tropical North Pacific by Rue *et al.* (1996) where approximately 30 % of Cr(VI) was reduced to Cr(III) with most of the reduced Cr being scavenged and removed.

Chromium remobilization can occur at the seawater-sediment interface due to release from biogenic particles during organic matter degradation. In coastal areas, high productivity can lead to increased input of organic carbon to the sediments which can quickly outpace the supply of oxygen available for respiration. Organic matter diagenesis can lead to the production of reduced species such as S^{-2} and Fe^{2+} (Froelich *et al.*, 1979), these reductants can readily convert Cr(VI) to Cr(III) in interstitial waters. The resulting Cr(III) can form organic chromium complexes; it can also be converted to Cr(VI), with the kinetics of this reaction enhanced by Mn oxyhydroxides (Schroeder and Lee, 1975). These processes can lead to elevated values near the sediment-water interface. Cr enrichment near the bottom waters was also evident in the coastal areas of Villefranche Bay, France (Gaillard *et al.*, 1986). The pore water data showed an enrichment in Cr as well as the presence of Mn-oxides at the top of the core. Thus diffusion of Cr from pore waters was a likely explanation for the observed bottom water values. In addition, increase in bottom water Cr can occur through ion-exchange reactions from particles introduced through atmospheric and fluvial deposition of the products of continental weathering. For instance,

mineral dusts deposited on the sea surface by the Atlantic north east winds were cited as a major source of Cr for the underlying deep-sea sediments (Chester, 1986).

3.4.8 Summary and Conclusions

This study of Cr species distribution in coastal and open ocean environments suggests that several processes control the geochemical behavior of this element. Labile Cr(III) concentrations in the open ocean are low (less than 5 % of total labile Cr) and closer in agreement with thermodynamic predictions. However, in the coastal inlets, this species is much higher, at 12-16 % of total labile Cr. The higher labile Cr(III) and total labile Cr values in coastal areas likely result from enhanced input through rivers coupled to chromium-organic matter interactions either via chromate reduction by DOM or formation of photodegradable organochromium complexes. Horizontal transport of Cr along isopycnals does not seem to be an important factor in this process.

Results of this study confirm the general features of Cr oceanic distribution: slight surface depletion, more or less invariant intermediate water values and a modest increase near the sediment-water interface. The surface depletion could be from Cr involvement in the biogeochemical cycles of the oceans but Cr association with either of the major nutrients is not clear, particularly in the data from the central North Atlantic. Other factors such as photoredox processes may be important in regulating Cr concentrations particularly in nearshore environments. Degradation of biogenic matter can result in Cr remobilization at the sediment-water interface.

Further studies of chromium behavior particularly in oligotrophic and also highly productive areas are required. Also needed are studies involving Cr concentrations and fluxes in interstitial waters of sediments to help constrain the specific controls on Cr geochemistry.

Chapter 4

The Annual Cycles of Chromium, Manganese and Iron in Saanich Inlet, B.C.

4.1 INTRODUCTION

Marine environments that display seasonal changes in their redox state offer a natural laboratory to study the processes responsible for the biogeochemical cycles of redox sensitive elements. Information on the factors responsible for the temporal and spatial cycling of elements is possible; in addition such a study affords the opportunity to track the importance of a particular process with time. This type of information is useful for predicting how trace and toxic elements respond to geochemical changes in the environment.

Various studies on the cycling of trace elements across oxic-anoxic environments in marine and lacustrine systems have been reported (e.g. Sholkovitz *et al.*, 1982; Kremling, 1983; Davison and Tipping, 1984; Jacobs *et al.*, 1985, 1987; Morfett *et al.*, 1988; Green *et al.*, 1989; Seyler and Martin, 1989; Van der Weijden *et al.*, 1990; Emerson *et al.*, 1979; Landing *et al.*, 1991; Lewis and Landing, 1991; Balistrieri *et al.*, 1992a, b; Johnson *et al.*, 1992; Pedersen *et al.*, 1993; Balistrieri *et al.*, 1994). The cycling of Fe and Mn across redox sensitive boundaries has received considerable attention in many of these studies mainly because of the central role these elements play in the cycling of other elements. Good data sets on the response of Cr to variations in environmental conditions are, however, relatively scarce. This can be attributed, in part, to the difficulty of measuring Cr species reliably without alteration.

Two recent studies in lake systems have provided insights into the cycling of this element across redox gradients. Balistrieri *et al.* (1992b) measured dissolved and particulate Cr, but not the two oxidation states, in Lake Sammamish, Washington, USA. They found that Cr was removed in bottom waters during sub-oxic and anoxic conditions although no specific mechanism was invoked. The study of chromium speciation and cycling in Lake Greifeensee, Switzerland reported that Cr(VI) was the predominant species even under anoxic conditions (Johnson *et al.*, 1992). Only under extremely reducing conditions, in the presence of S(-II) and Fe(II), was the reduction of Cr(VI) observed yielding mostly colloidal Cr(III) forms.

This study focuses on the speciation and cycling of Cr, Fe and Mn over an annual cycle in Saanich Inlet, a seasonally anoxic inlet, located on Vancouver Island, B.C. Canada. The cycle of spring/summer oxygen depletion and deep water renewal in fall makes this an ideal location to examine the geochemical processes affecting the behavior of redox-sensitive elements. Several studies on the speciation of various elements during the stratified summer months, in the inlet, have been reported (e.g. Emerson *et al.*, 1979; Cranston, 1979; Jacobs and Emerson, 1982; Cutter, 1982). This is, however, the first study in this fjord in which the redox-driven cycling of several trace elements have been followed through the course of an entire annual cycle of deep water oxygen depletion and renewal.

4.2 METHODS AND MATERIALS

4.2.1 Study Site

Saanich Inlet is an intermittently anoxic fjord located on the south-eastern coast of Vancouver Island, B.C., Canada (Figure 4.1). It is 25 km in length, 7.2 km at its widest part, and is connected to Haro Strait in the east and Georgia Strait in the north-east by Satellite Channel. Water exchange is restricted by a well defined sill (~ 75 m) at the mouth of the inlet between Moses Point and Hatch Point. Beyond this shallow entrance, the floor deepens to a maximum of 232 m off Sheppard Point. It shoals gradually toward Squally Reach (~ 180 m) and finally rises rapidly towards the Goldstream River.

The drainage basin of the inlet is small and situated in a rain-shadow, so that it contributes little water run-off (Herlinveaux, 1962). The Goldstream River, situated at the head of the fjord, is the largest stream entering the inlet directly; however, its discharge is small ($0.85 \text{ m}^3/\text{sec}$; Herlinveaux, 1962). Most of the fresh-water run-off reaching Saanich Inlet comes from the Cowichan River, flowing into Cowichan Bay, situated about 6 km north-west of the sill (Figure 4.2.1). Its discharge follows the seasonal precipitation pattern, with a maximum in December (~ $90 \text{ m}^3/\text{sec}$) and a minimum in August ($5\text{-}10 \text{ m}^3/\text{sec}$), although large fluctuations have been observed over short periods.

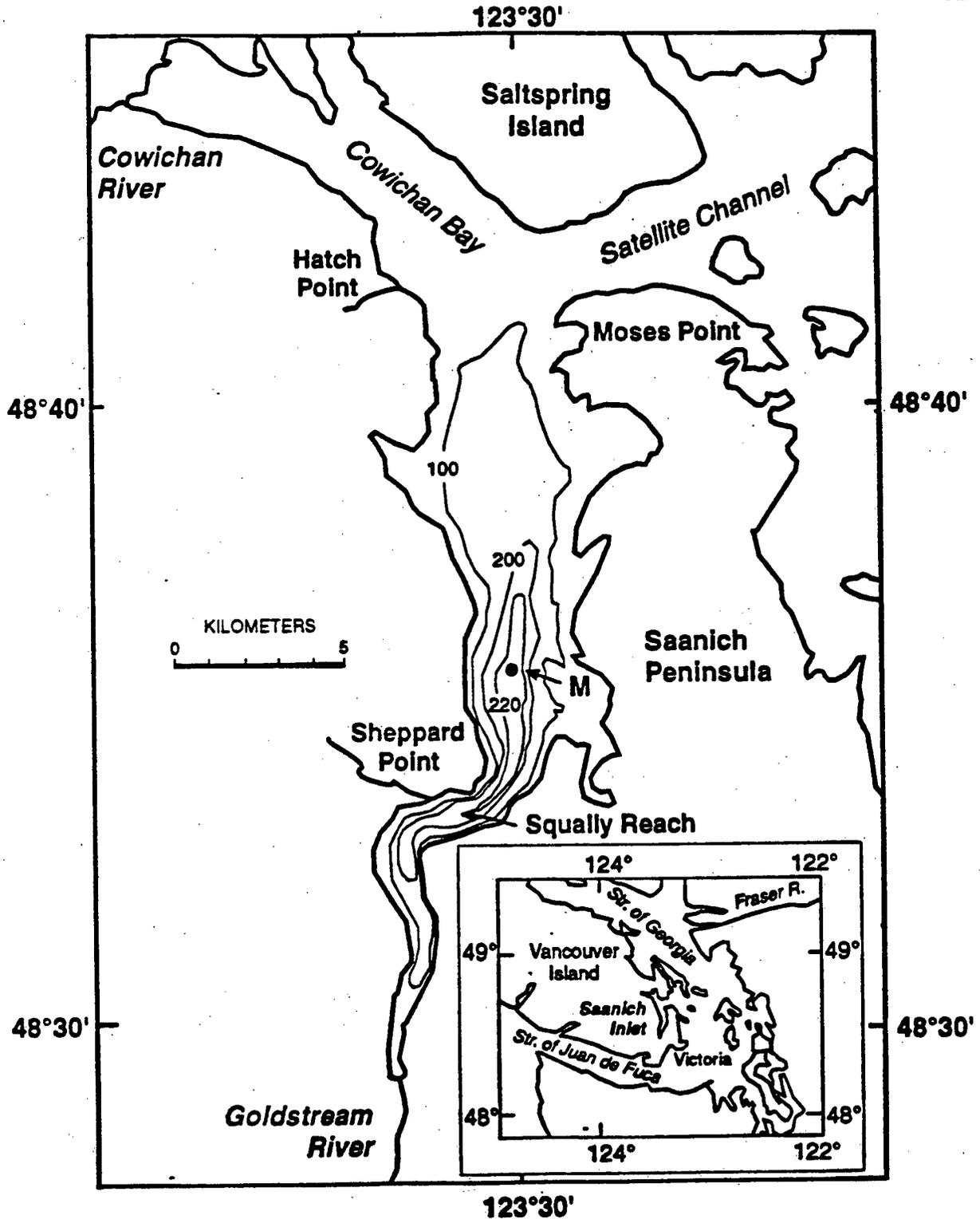


Figure 4.1 Saanich Inlet, British Columbia, located on the southeast side of Vancouver Island. A total of thirteen vertical profiles representative of the seasonal flushing cycle of the Inlet were obtained between May 1994 and July 1995.

The surface waters are also influenced by the fresh water discharge from the Fraser River, which is at its maximum in June. Each summer, a low-salinity, silt-laden water mass moves towards the Gulf Islands and enters Saanich Inlet through Satellite Channel, producing a surface dilution which is generally evident down to 50 m depth (Waldichuk, 1957; Herlinveaux, 1962). In Saanich Inlet, this type of circulation seems very weak and sporadic (Herlinveaux, 1962, 1966, 1972) and produces an effective exchange of surface water with nearby channels, but is not sufficiently developed to flush the deep basin of the inlet below sill-level. Consequently anoxic conditions are gradually established in the late winter, spring and early summer as oxygen consumption by organic matter decomposition after the vernal plankton bloom exceeds renewal by mixing in of oxygen-rich water.

In late summer or early fall, a dense, well-oxygenated body of water is produced in Haro Strait by intensive tidal mixing of warm, low-salinity surface water from the Strait of Georgia with cold, saline, upwelled water derived from the California undercurrent. Some of this dense, oxygenated water finds its way to Saanich Inlet reaching Satellite Channel almost undiluted since at this time input from the Cowichan is at its minimum. It is then able to displace some of the less dense water at the bottom of the inlet. Flushing seems to occur in boluses of dense water which spill mainly during flood tides (Anderson and Devol, 1973). This water renewal takes place during most years; however, the extent of flushing varies widely from year to year. When little flushing occurs, stronger anoxic conditions develop during the following spring.

The formation of anoxic deep water has a profound effect on many biological and chemical systems. As the organic matter decomposes, it utilizes oxygen, nitrate, and sulfate. Various reduced nitrogen species and hydrogen sulfide are among the products of these reactions. The distributions of trace metals such as Mn, Fe and Cr, which can also participate as terminal electron acceptors in organic matter diagenesis or be reduced by the byproducts of microbial processes, are therefore greatly affected.

4.2.2 Sampling and Analytical Methods

A total of thirteen vertical profiles representative of the seasonal flushing cycle of the Inlet were obtained between May 1994 and July 1995. Sampling was conducted aboard the C.S.S. Jager from the Institute of Ocean Sciences, Sidney, B.C. Samples were collected using Teflon[®]-lined 10 L Go-Flo bottles suspended on a Kevlar[®] line at station 'M' (Figure 4.1). The bottles, which had previously been acid-washed, were triggered using Teflon[®] messengers.

Immediately after the Go-Flo bottle was brought onboard, subsamples for dissolved oxygen were drawn using an acid-washed Teflon[®] tube with particular care being taken to preserve anoxia in samples from depth. The O₂ bottles were first flushed with the seawater sample, overfilled and the water preserved on the boat with Winkler reagents. Standard Winkler titrations were carried out in the laboratory. Seawater samples for Cr species determinations were either processed on board or were preserved for later processing in the shore-based laboratory. The preservation technique involved quick freezing using an acetone-dry ice mixture which froze the samples in less than five minutes. This method of sample treatment was effective in preservation of speciation as long as the time between thawing out and analysis was kept to a minimum (under one hour).

Seawater samples for dissolved and particulate Mn and Fe were collected in acid - washed LDPE bottles and filtered through 0.45 µm acid - washed polycarbonate filters (Nuclepore) in the shore - based laboratory (4 - 8 hours after sampling); they were then acidified to pH 1.5 with 8 N doubly-quartz distilled HNO₃ (Seastar Chemicals, Sidney, B.C.). A comparison with samples filtered on the boat immediately after collection shows negligible loss of Fe(II) due to possible oxidation artifacts.

The procedure for Cr determination using electron capture detection gas chromatography (ECD-GC) has been described elsewhere in detail (Mugo and Orians, 1993). This liquid-liquid extraction technique uses 1,1,1-trifluoro-2,4-pentanedione (Htfa) to chelate free (uncomplexed) Cr(III) from a 15 mL seawater sample with toluene as the solvent (this is referred to as "labile" Cr(III)). Sodium sulfite serves to reduce Cr(VI) to labile Cr(III) in a separate 15 mL sample, thus

allowing determination of "total labile" Cr as Cr(III). Cr(VI) is then obtained by difference. To determine the fraction of bound Cr (presumably in colloidal and/or organic forms) modifications were made to the procedure similar to those reported by Cutter (1982) and Ahern *et al.* (1985). To a third 15 mL seawater sample acidified to pH 2.3 with 6 N Q-HCl (Seastar Chemicals, Sidney, B.C.), 200 μ L of 30 % hydrogen peroxide solution was added and the sample heated in the microwave oven for a total of 5 min with regular shaking and release of pressure. The sample bottle was then stirred with a Teflon[®] coated magnetic stirrer while being irradiated with UV light from a 275 W lamp for 1 hr. At the end of the period, sample was allowed to cool, the sodium sulfite reducing agent added, and the pH raised to 6.0 ± 0.2 with NaAc/HAc buffer. Chromium was then extracted and analyzed using the ECD-GC technique. The Cr concentration in this sample is referred to as "total oxidizable" Cr. The difference between "total oxidizable" Cr and the "total labile Cr" constitutes an estimate of the bound (presumably as colloidal/organic) Cr fraction referred to as the "non-labile" Cr fraction.

Dissolved Mn and Fe were measured a Varian Spectra AA300/400 AAS equipped with a Varian Techtron GTA-96 graphite-tube atomizer and Zeeman background correction. Samples were diluted (10-500 fold) with acidified DDW either on the bench or through instrumental pre-programming, and delivered to the furnace using a Varian Techtron PSC-56 programmable autosampler. Analysis was conducted using the method of standards addition. The suspended material on the polycarbonate filters was subjected to treatments with NH_4OH (Seastar Chemicals, Sidney, B.C.) to destroy the filters, followed by microwave-assisted digestion of residual material with 0.5 mL each of Seastar Q-HCl, Q- HNO_3 and Q-HF in sealed Teflon bombs. The final acid mixtures were taken to dryness on a hot plate inside a laminar flow hood in the clean laboratory, then redissolved in 4 mL of 2 N Q- HNO_3 . Analyses were also performed by GFAAS using the method of standards additions. The analytical methods, precision of the analyses as well as detection limits and procedural blanks are summarized in Table 4.2.2.1.

Component	Technique	Precision ^a	D.L ^b
Dissolved O ₂	Titration ^c	±2%	5.0 µM
Labile Cr(III)	ECD-GC ^d	±3%	0.06 nM
Total labile Cr	ECD-GC ^d	±2%	0.20 nM
Total oxidizable Cr	ECD-GC ^e	±5%	0.21 nM
Dissolved Mn	GFAAS	±6%	11 nM
Particulate Mn	GFAAS	±5%	2.5 nM
Dissolved Fe	GFAAS	±8%	16 nM
Particulate Fe	GFAAS	±5%	8.3 nM
Particulate Al	GFAAS	±6%	10 nM

^aBased on triplicates, ^bDetection limit-defined as $3\sigma_{n-1}$ of the blank ^cCarpenter, (1965), ^dMugo and Orians (1993), ^eSee modifications to ECD-GC technique in text.

Table 4.2.2.1 Analytical techniques, precision and detection limits for the methods used for seawater samples from Saanich Inlet.

4.3 RESULTS AND DISCUSSION

4.3.1 Time-Depth Contours and Vertical Profiles

Temporal and spatial patterns of the measured chemical properties in Saanich Inlet between May 1994 and July 1995 are presented in time-depth contours (Figures 4.2-4.8) to provide an overview of the yearly cycle. Details of the processes that control the speciation and distribution of each trace element are more thoroughly addressed using monthly concentration-depth profiles for the particular elements (Figures 4.9-4.21).

4.3.2 Water Column Redox Conditions

The time-depth cycle of oxygen (Figures 4.2 and 4.9-4.21) reveals several features. Dissolved oxygen concentrations are high in the oxic zone above 70 m (220-350 μM) throughout the cycle. The maximum concentrations occur in spring (maximum 350 μM in June 1994 and 330 μM in April 1995). This is likely from oxygen production during the spring bloom (photosynthesis). Similar effects have been reported by Balistrieri *et al.* (1992a) in their study of Lake Sammamish, Washington. Decomposition of organic matter throughout the water column or at the sediment-water interface is responsible for decreasing oxygen concentrations in the deep water. The suboxic zone (O_2 values 5-30 μM) at mid-depth extends from 110-140 m during stratification in the spring and early summer months. Samples below 140 m during this period are considered anoxic with no detectable oxygen (< 5 μM). Hydrogen sulfide was detected qualitatively (by smell) in samples from 160-200 m in May, June and July 1994, and also in July 1995.

In August, cooler air temperatures and greater mixing in the oxic zone results in oxygen detection deeper in the water column; the suboxic-anoxic boundary migrates to 160 m from 130 m during the previous month. It was, however, not until September when dissolved oxygen (13-27 μM) was detected in bottom water samples from 160, 180 and 200 m depths, which were previously anoxic. This resulted from the influx of dense, oxygenated water over the sill into the bottom of the inlet.

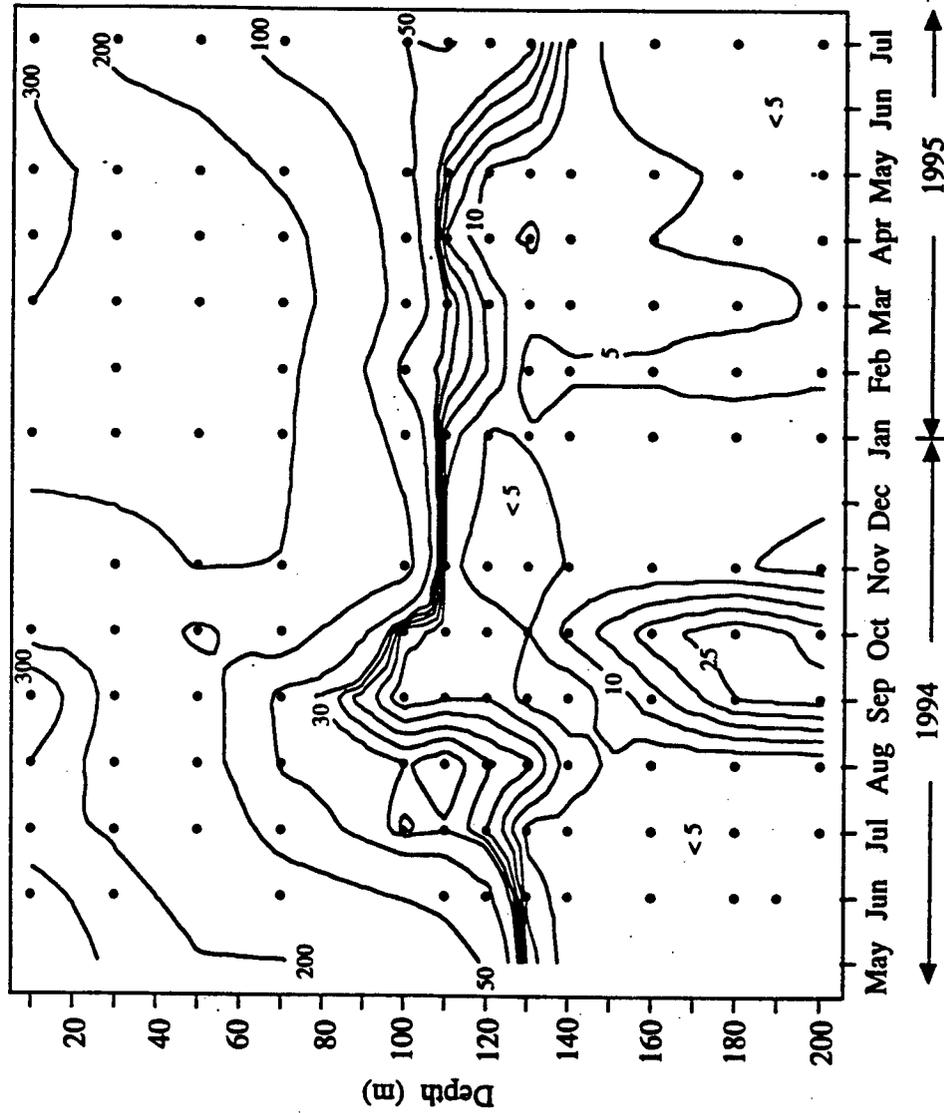


Figure 4.2 Dissolved oxygen (μM) time-depth distribution in Saanich Inlet for the period May 1994-July 1995.

This inflow of new water results in an upward displacement of the water above the depth of influx which results in a shallowing of the suboxic zone; seawater samples above 110 m and below 140 m thus showed higher oxygen concentrations. This flushing mechanism for the inlet was also observed by Anderson and Devol (1973). Dissolved oxygen in the bottom waters then decreases in the winter as organic matter is degraded without any new deep water inflow. The highest O₂ values measured for the bottom zone (25-29 μM) were in September and October during overturn. Annual deep water renewal has been estimated as 18-46 % based on nitrate budgets (Anderson and Devol, 1973).

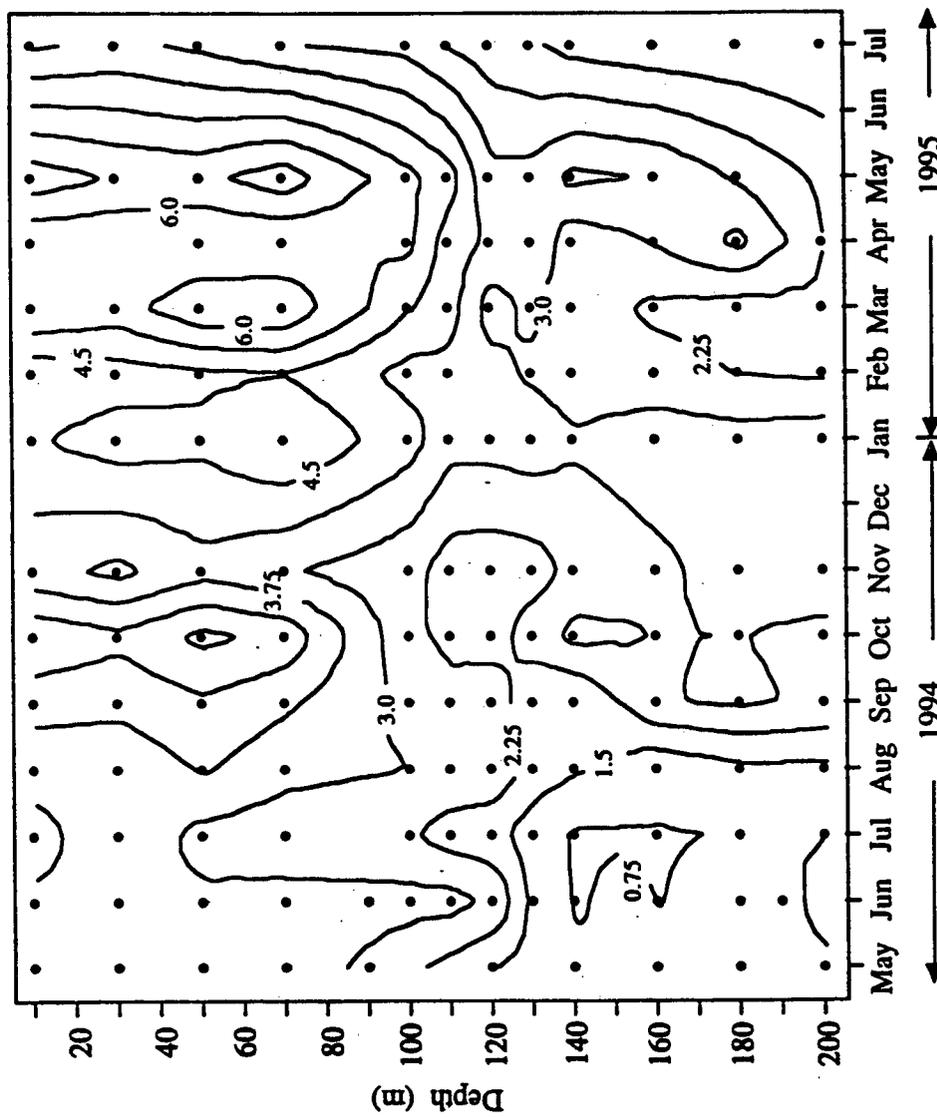


Figure 4.3 Total labile chromium (nM) time-depth distribution in Saanich Inlet for the period May 1994-July 1995.

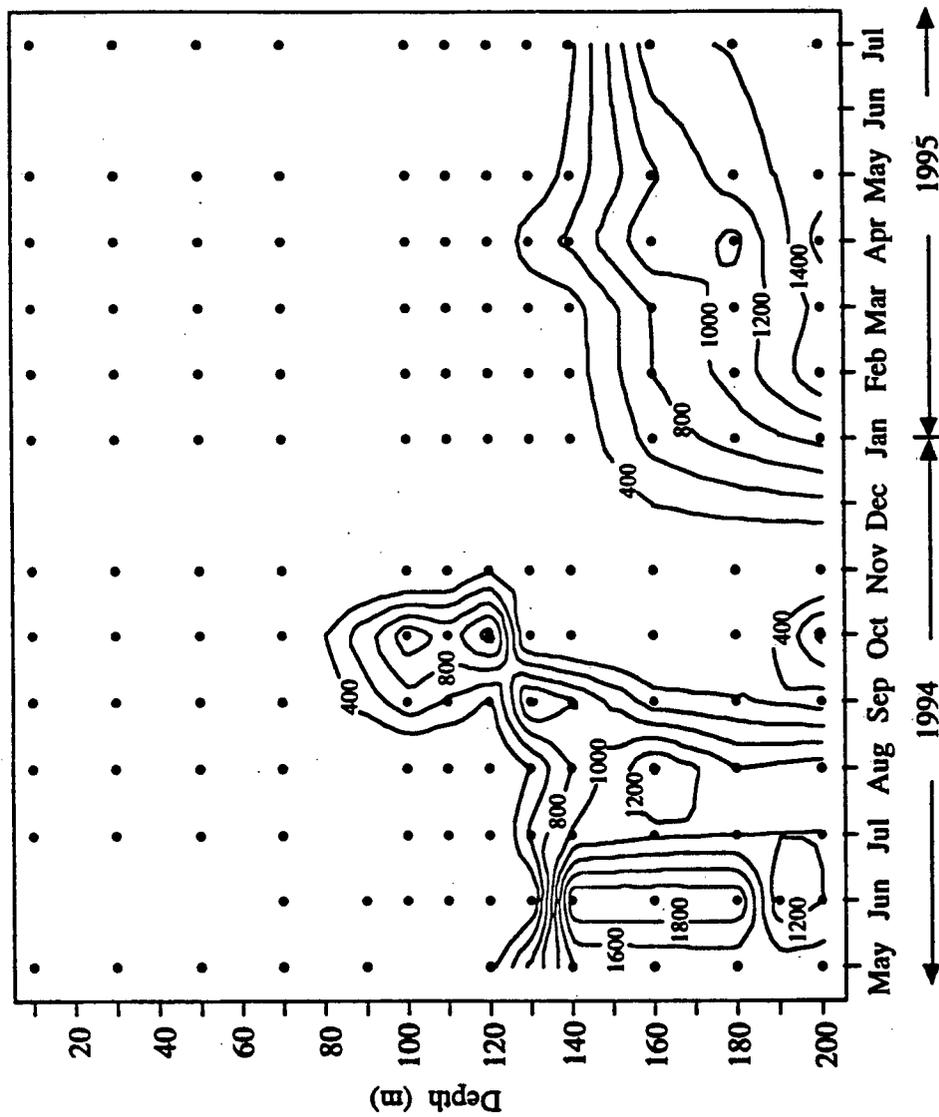


Figure 4.4 Dissolved manganese (nM) time-depth distribution in Saanich Inlet for the period May 1994-July 1995.

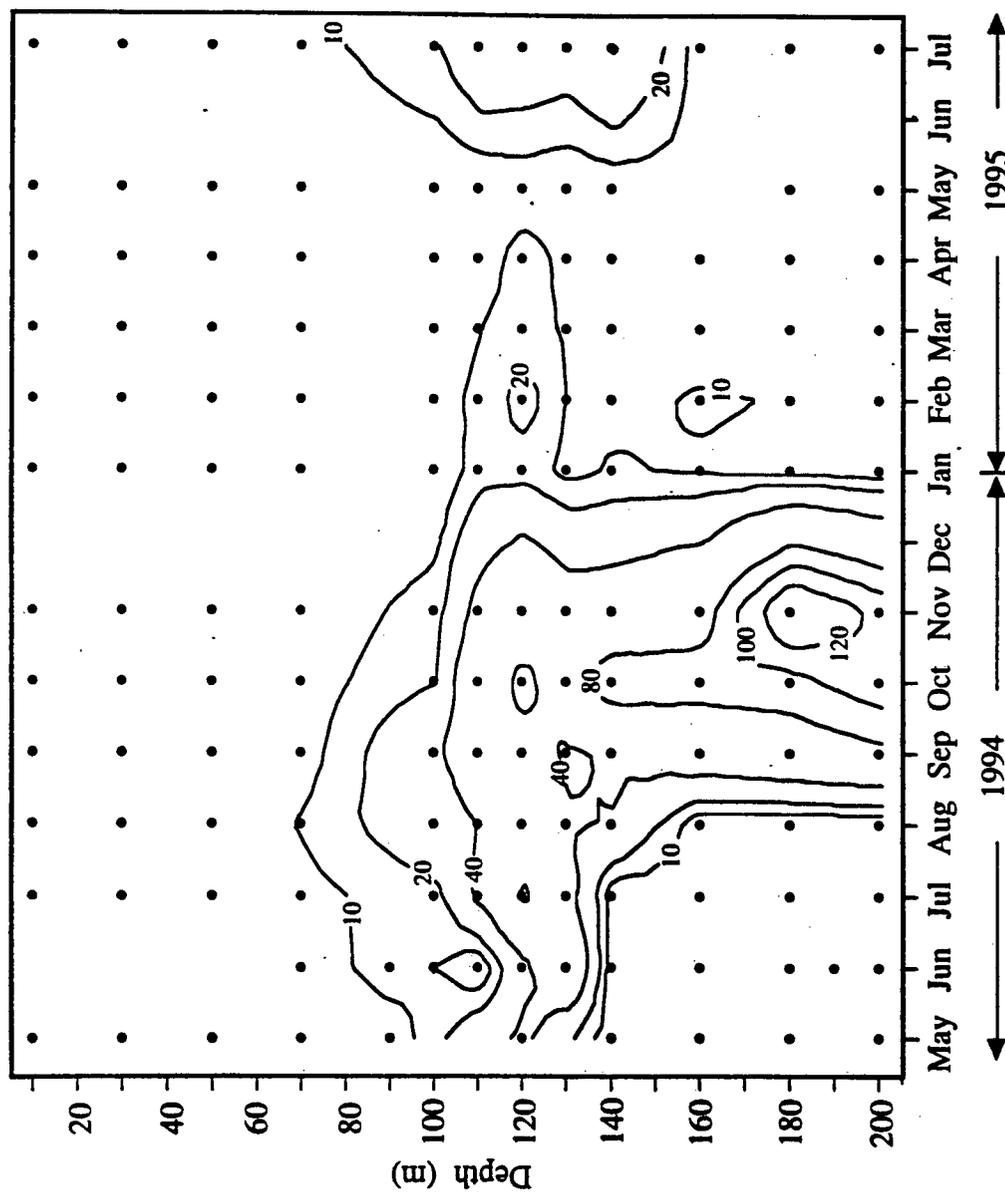


Figure 4.5 Particulate manganese (nM) time-depth distribution in Saanich Inlet for the period May 1994-July 1995.

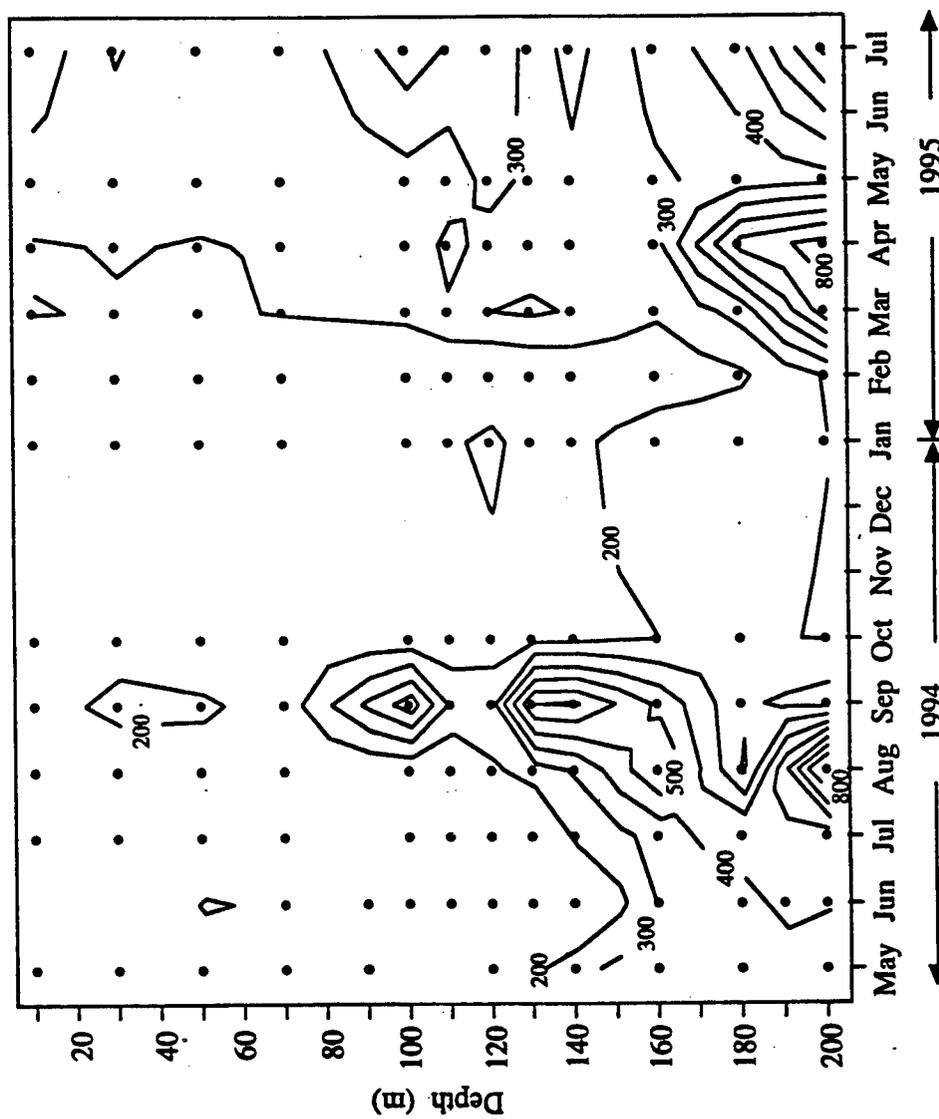


Figure 4.6 Dissolved iron (nM) time-depth distribution in Saanich Inlet for the period May 1994-July 1995.

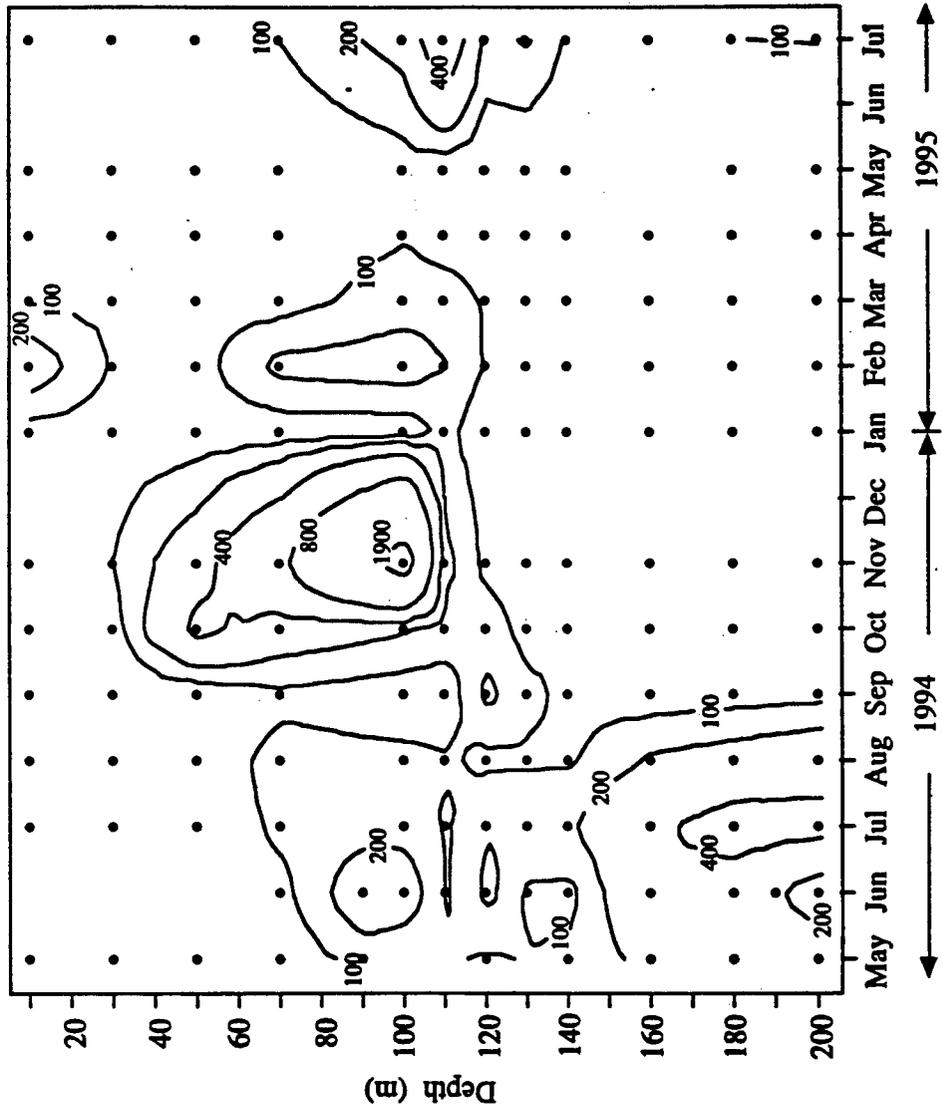


Figure 4.7 Particulate iron (nM) time-depth distribution in Saanich Inlet for the period May 1994-July 1995.

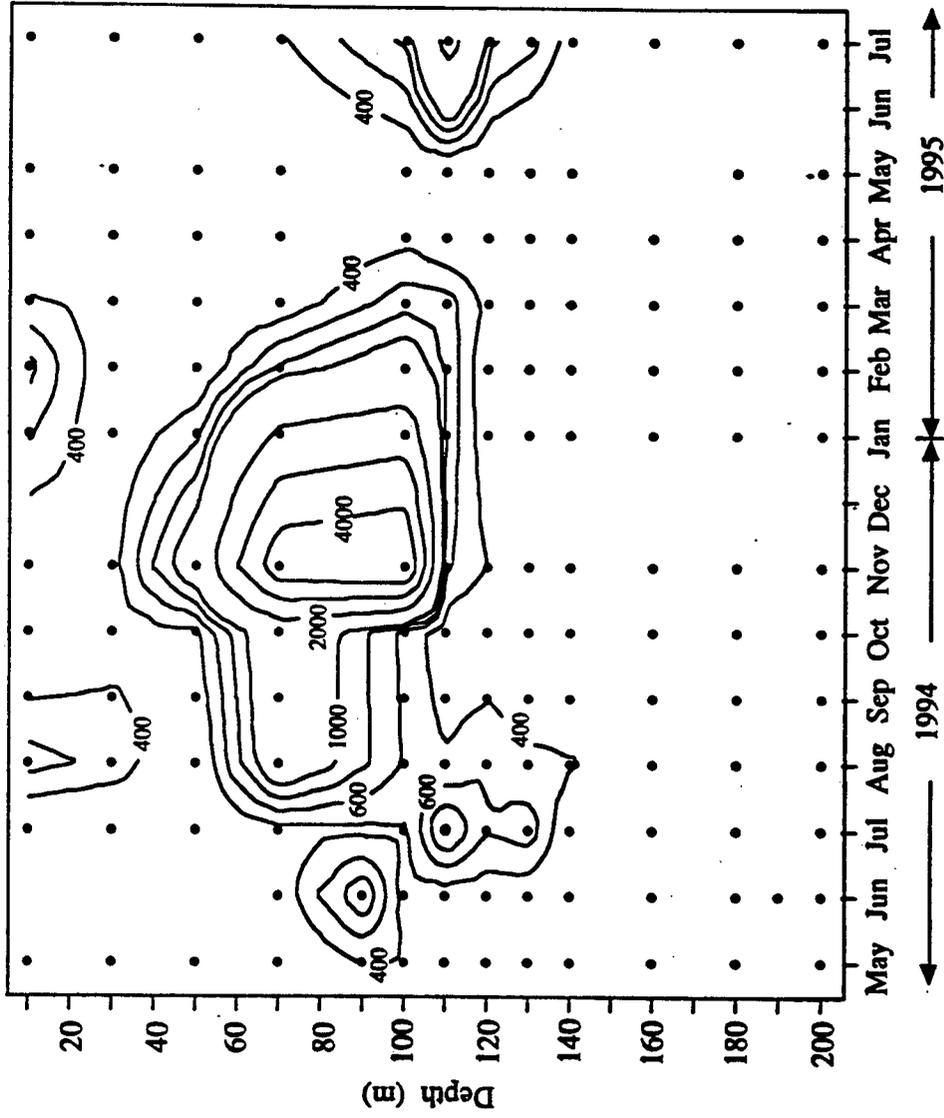


Figure 4.8 Particulate aluminum (nM) time-depth distribution in Saanich Inlet for the period May 1994-July 1995.

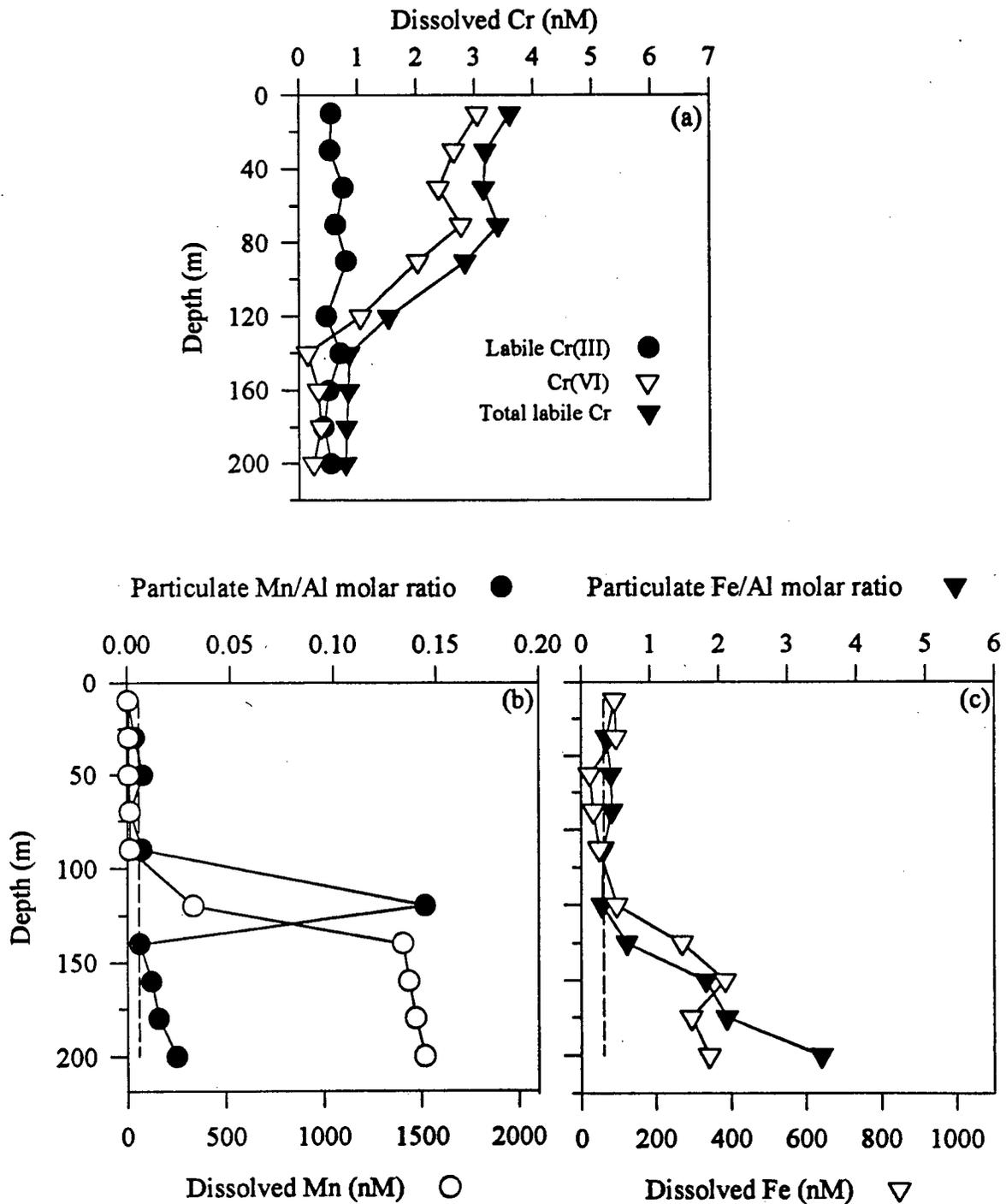


Figure 4.9: Saanich Inlet data for MAY 1994: (a) Chromium species (b) Dissolved and Particulate Mn/Al molar ratio (c) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (b) & (c) represent crustal metal/Al molar ratio.

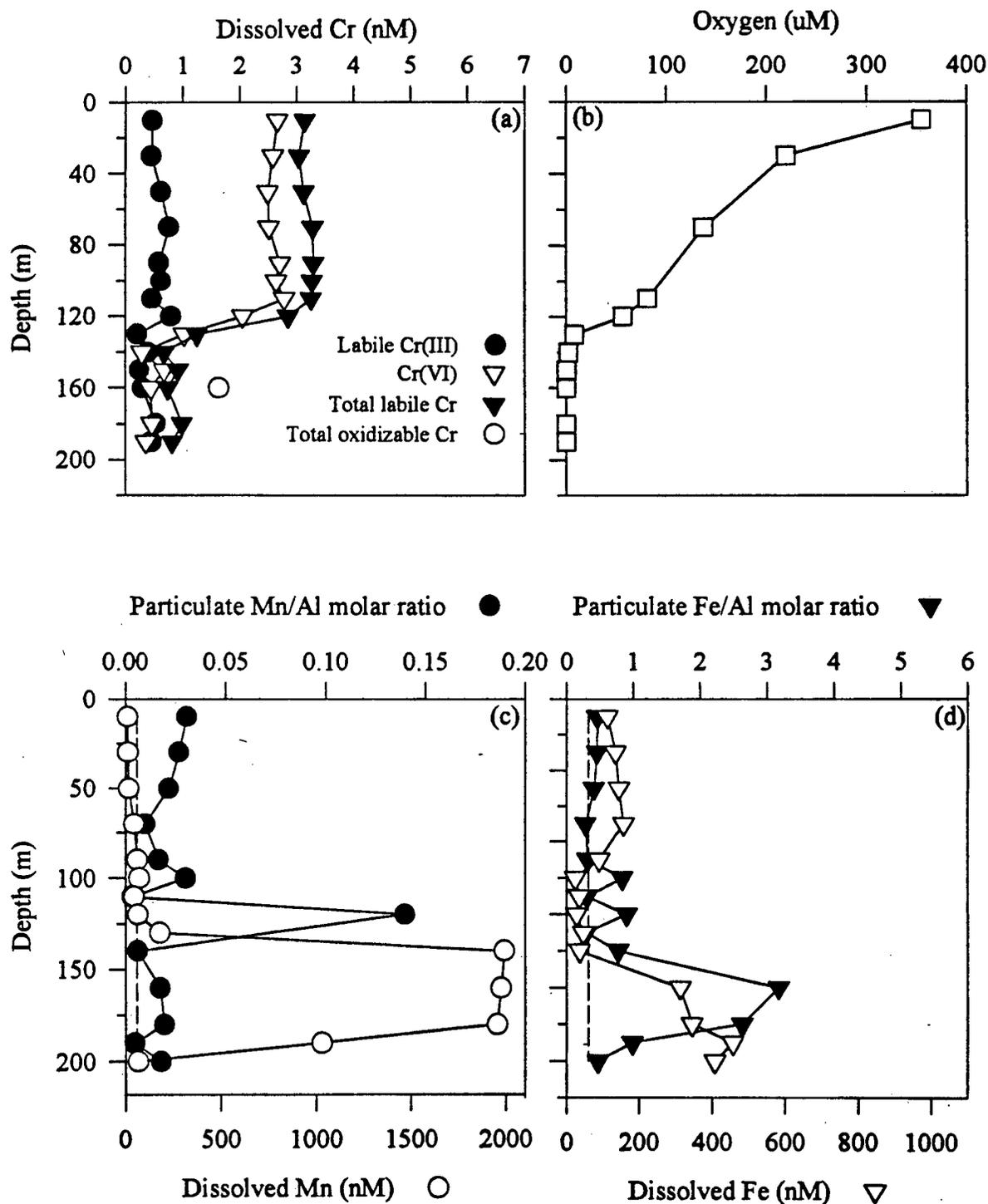


Figure 4.10: Saanich Inlet data for JUNE 1994: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

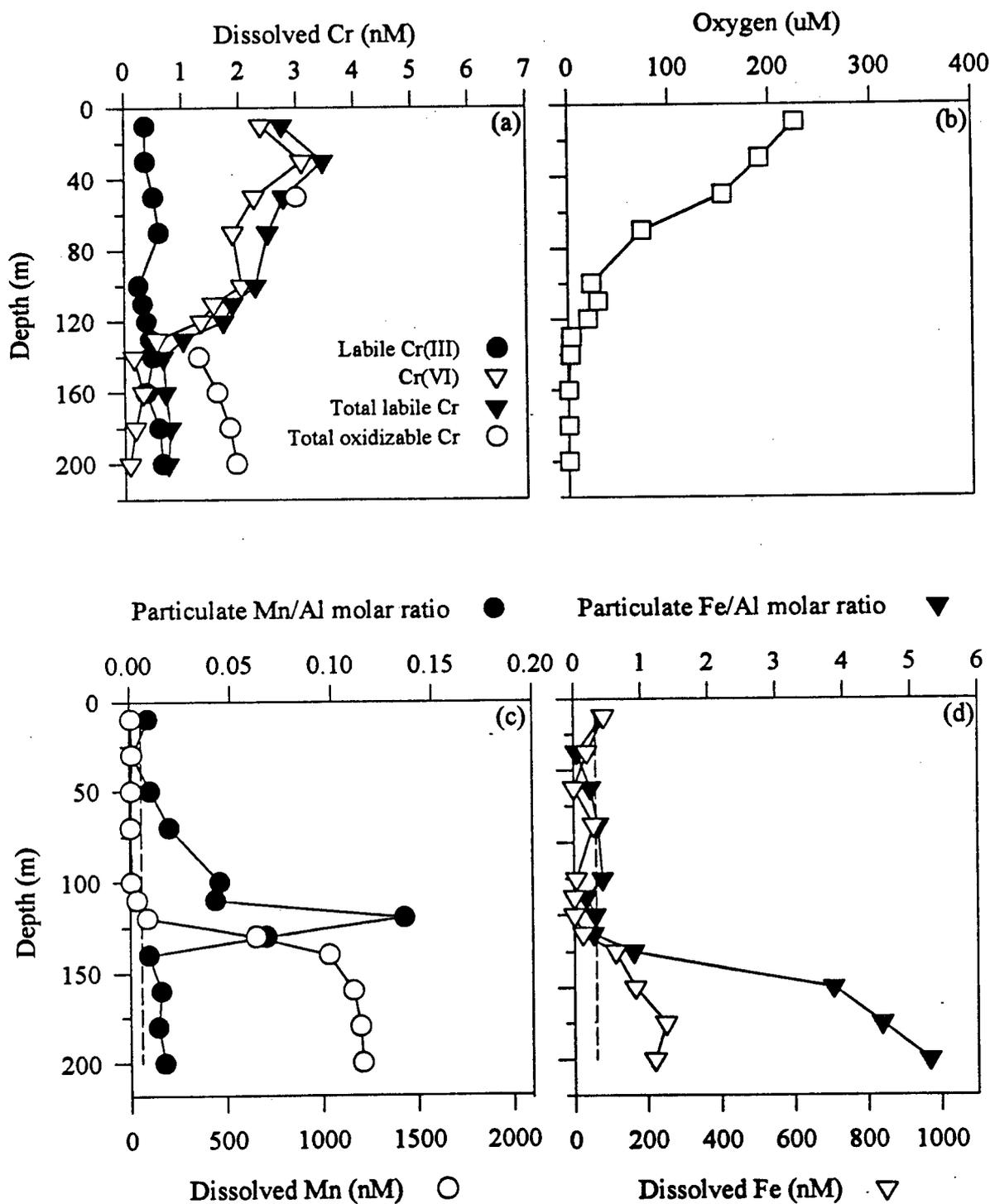


Figure 4.11: Saanich Inlet data for JULY 1994: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

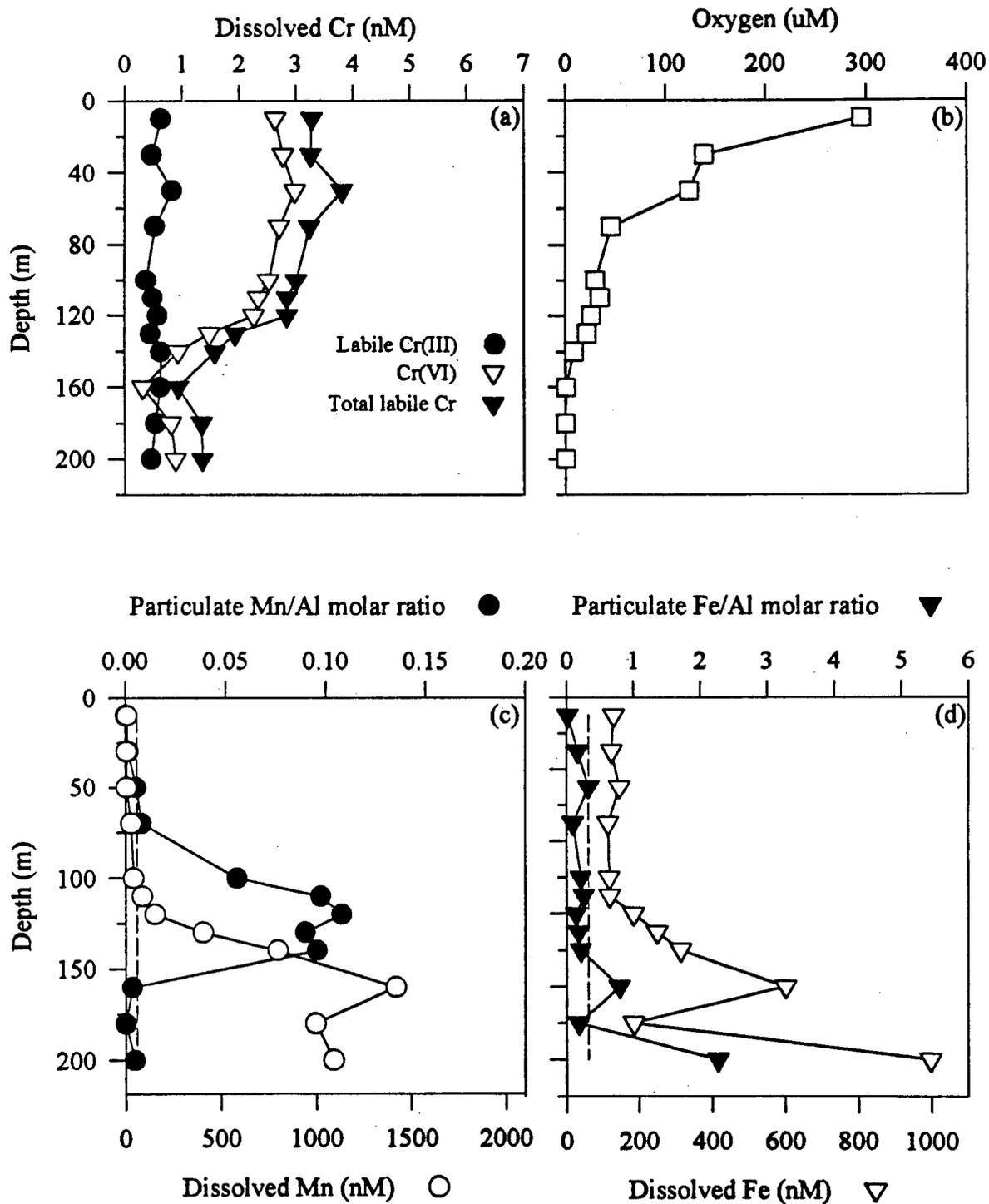


Figure 4.12: Saanich Inlet data for AUGUST 1994: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

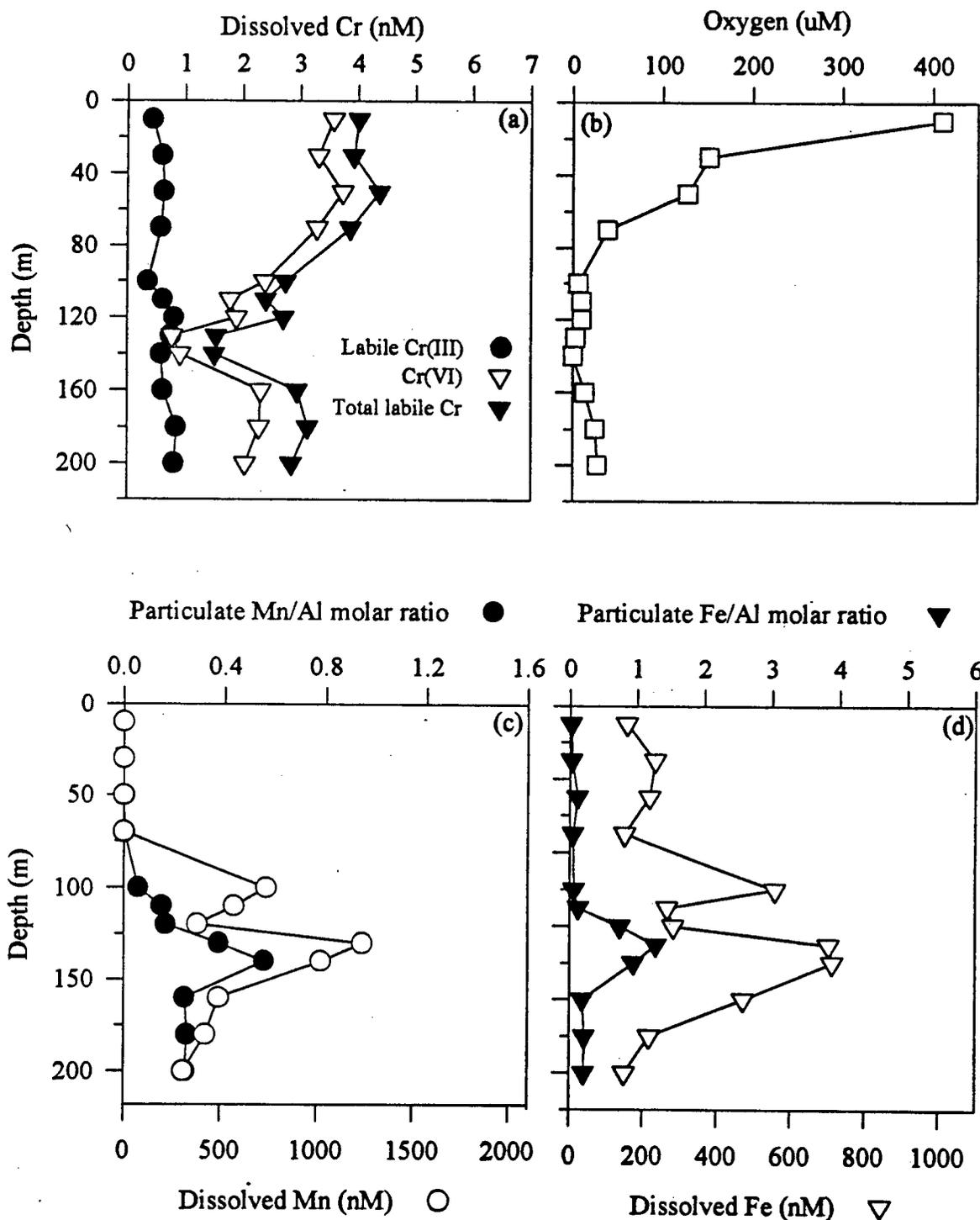


Figure 4.13: Saanich Inlet data for **SEPTEMBER 1994**: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

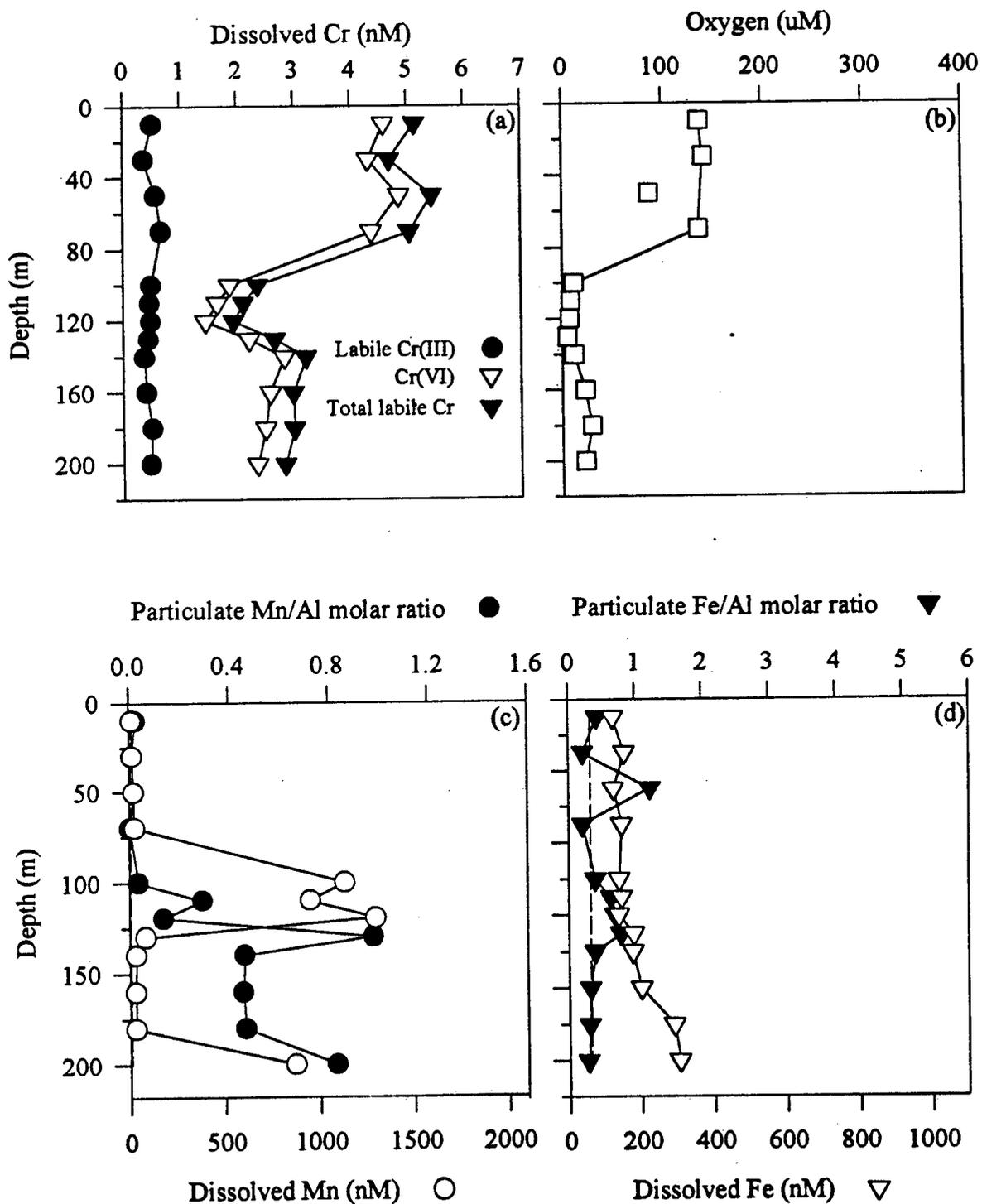


Figure 4.13: Saanich Inlet data for **OCTOBER 1994**: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

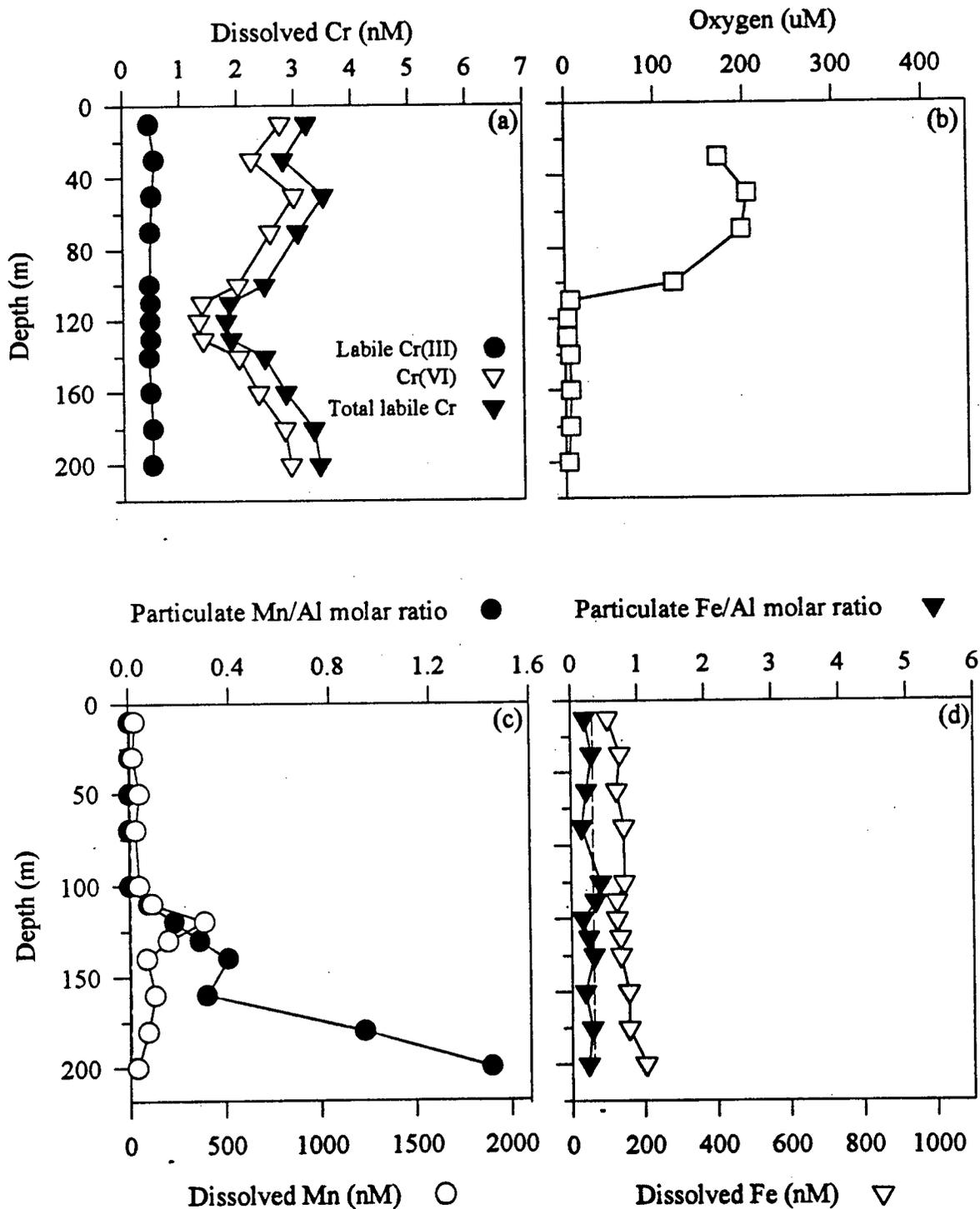


Figure 4.14: Saanich Inlet data for NOVEMBER 1994: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

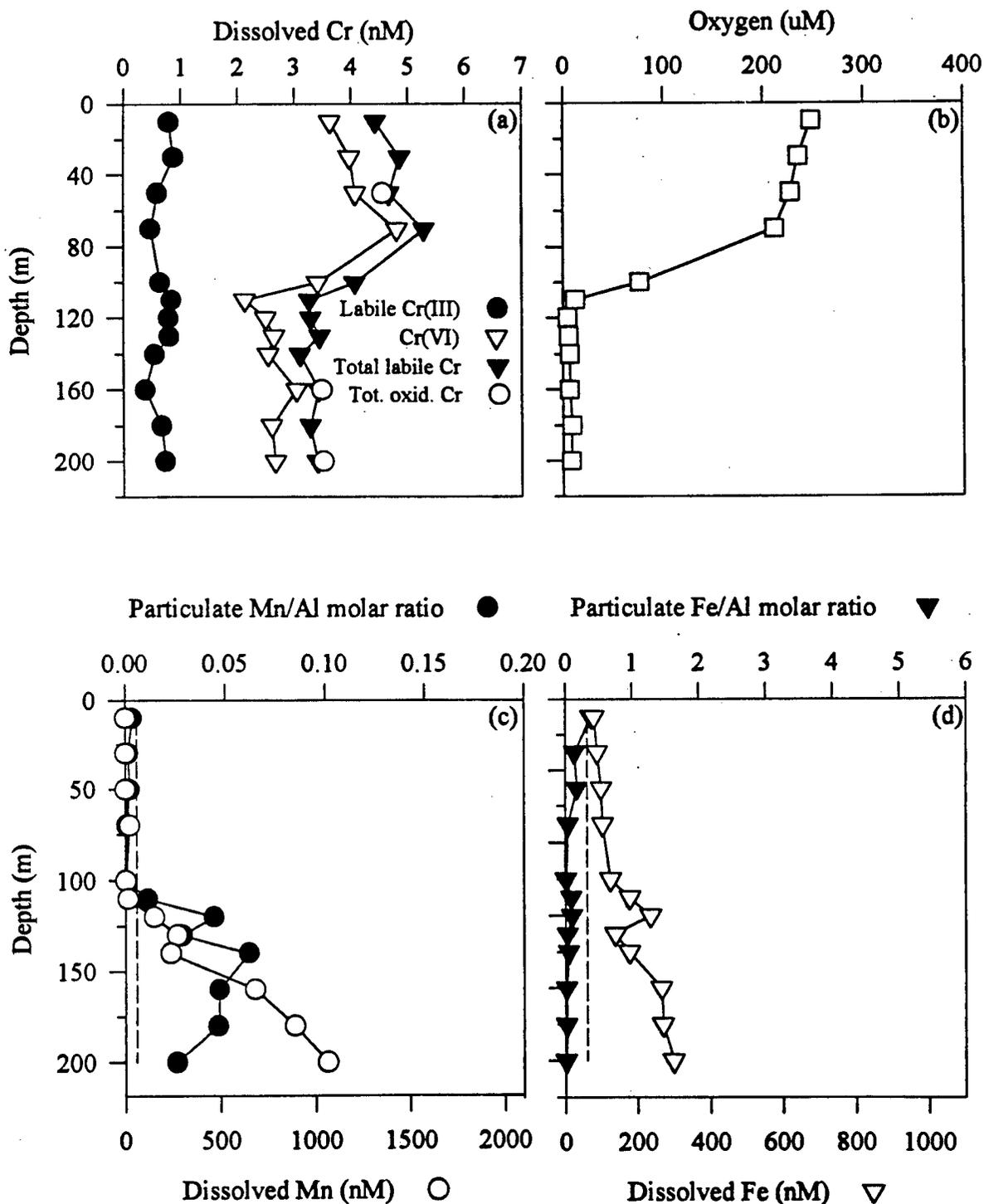


Figure 4.16: Saanich Inlet data for **JANUARY 1995**: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

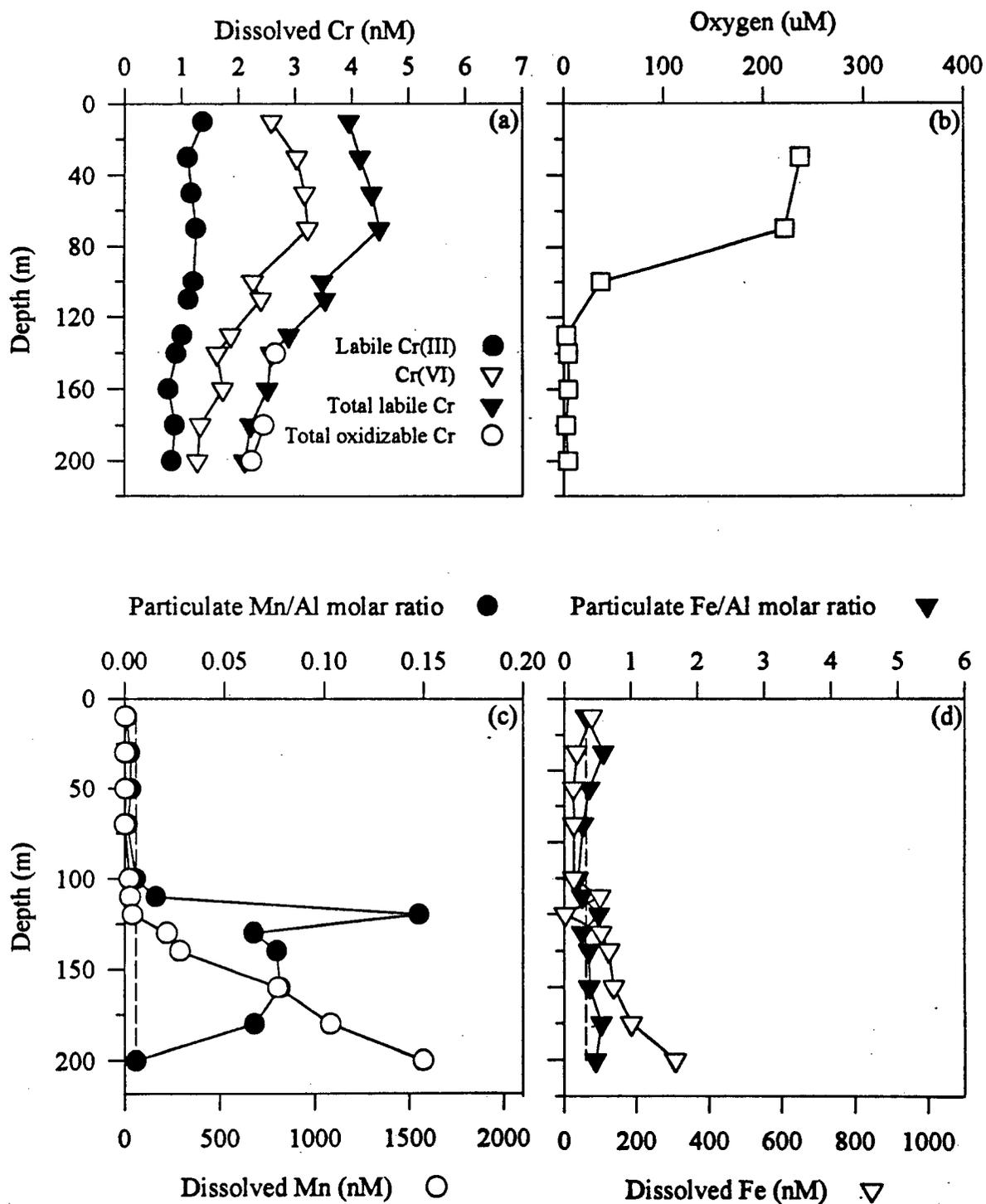


Figure 4.17: Saanich Inlet data for FEBRUARY 1995: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

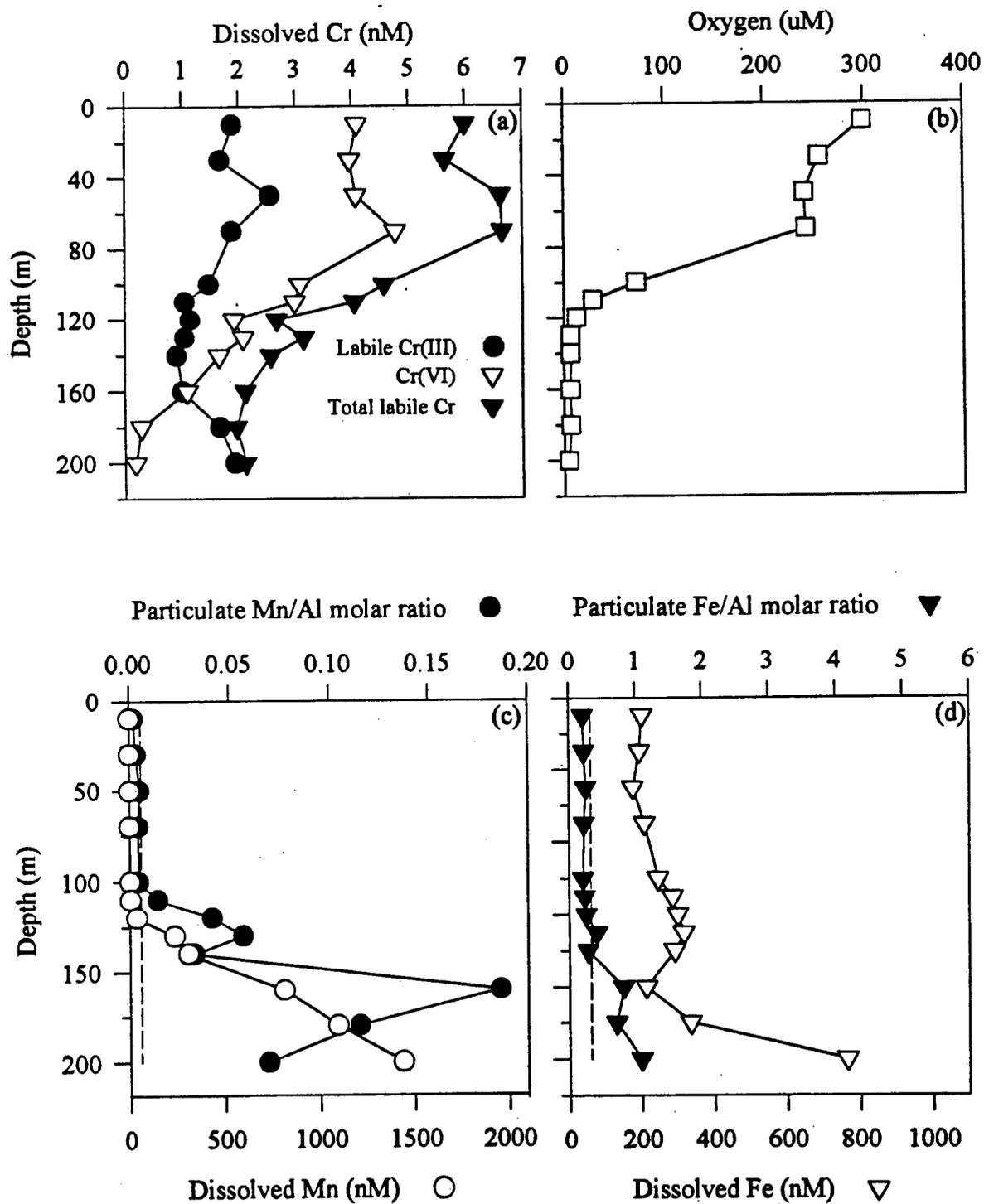


Figure 4.18: Saanich Inlet data for MARCH 1995: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

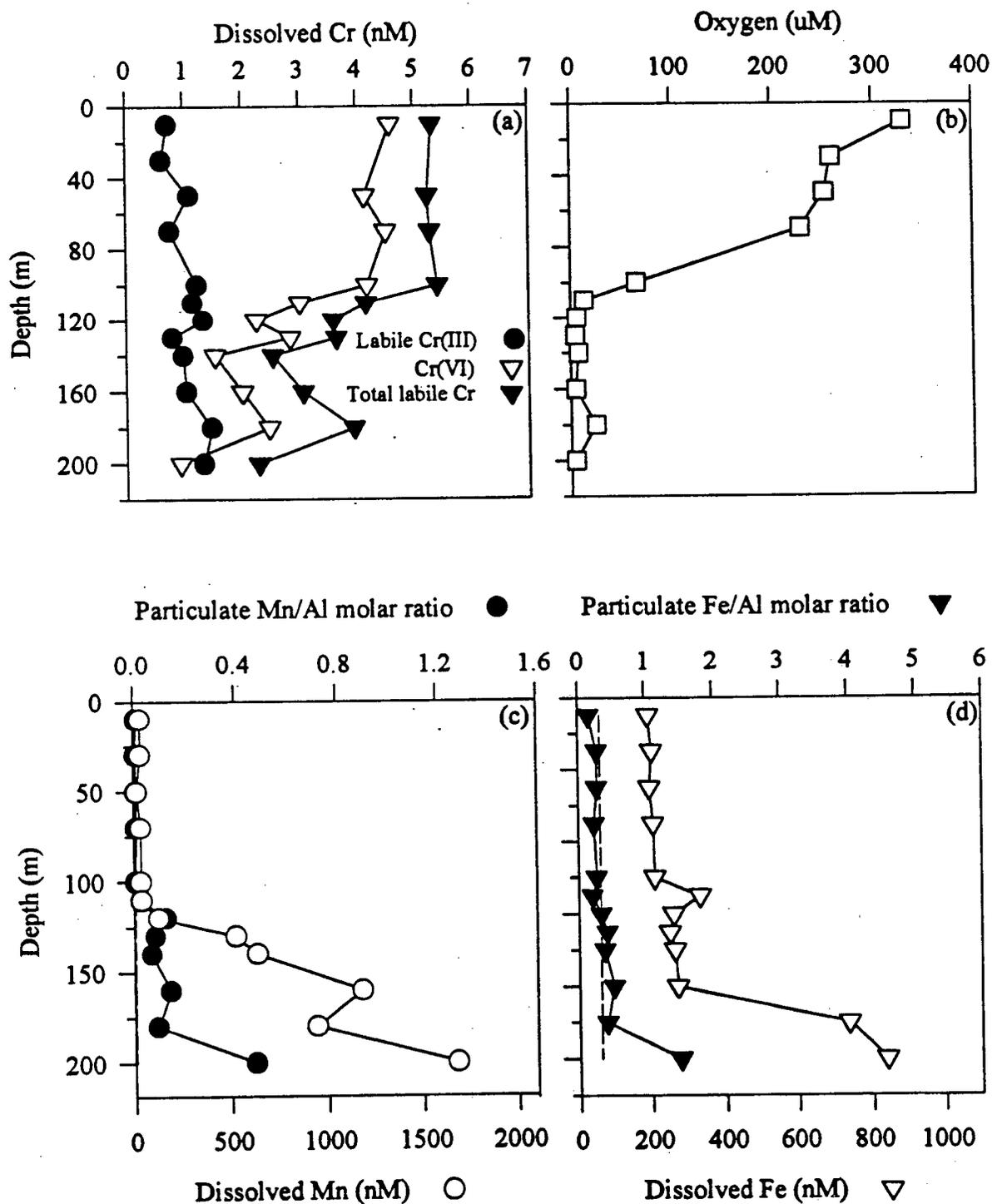


Figure 4.19: Saanich Inlet data for APRIL 1995: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

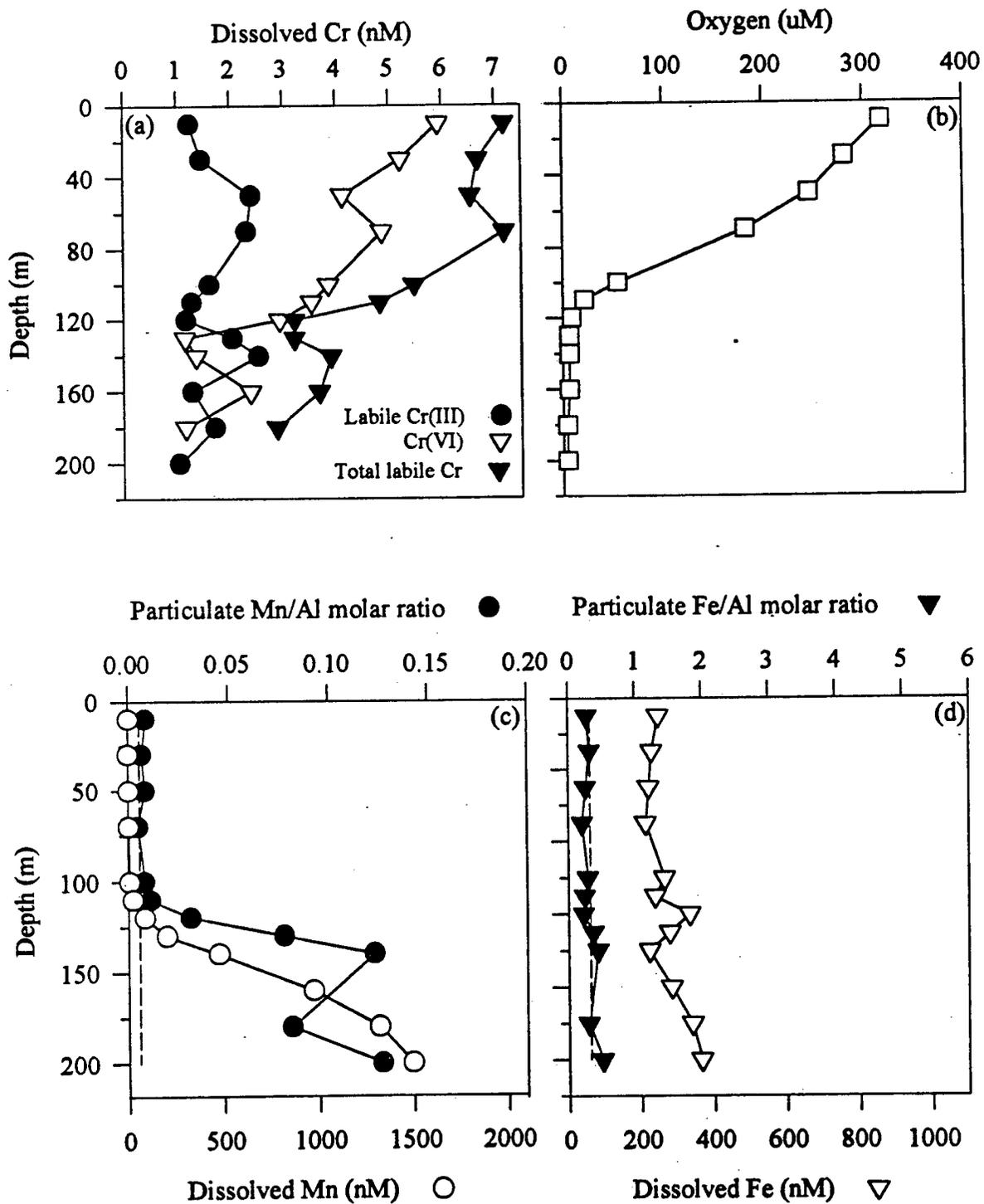


Figure 4.20: Saanich Inlet data for MAY 1995: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

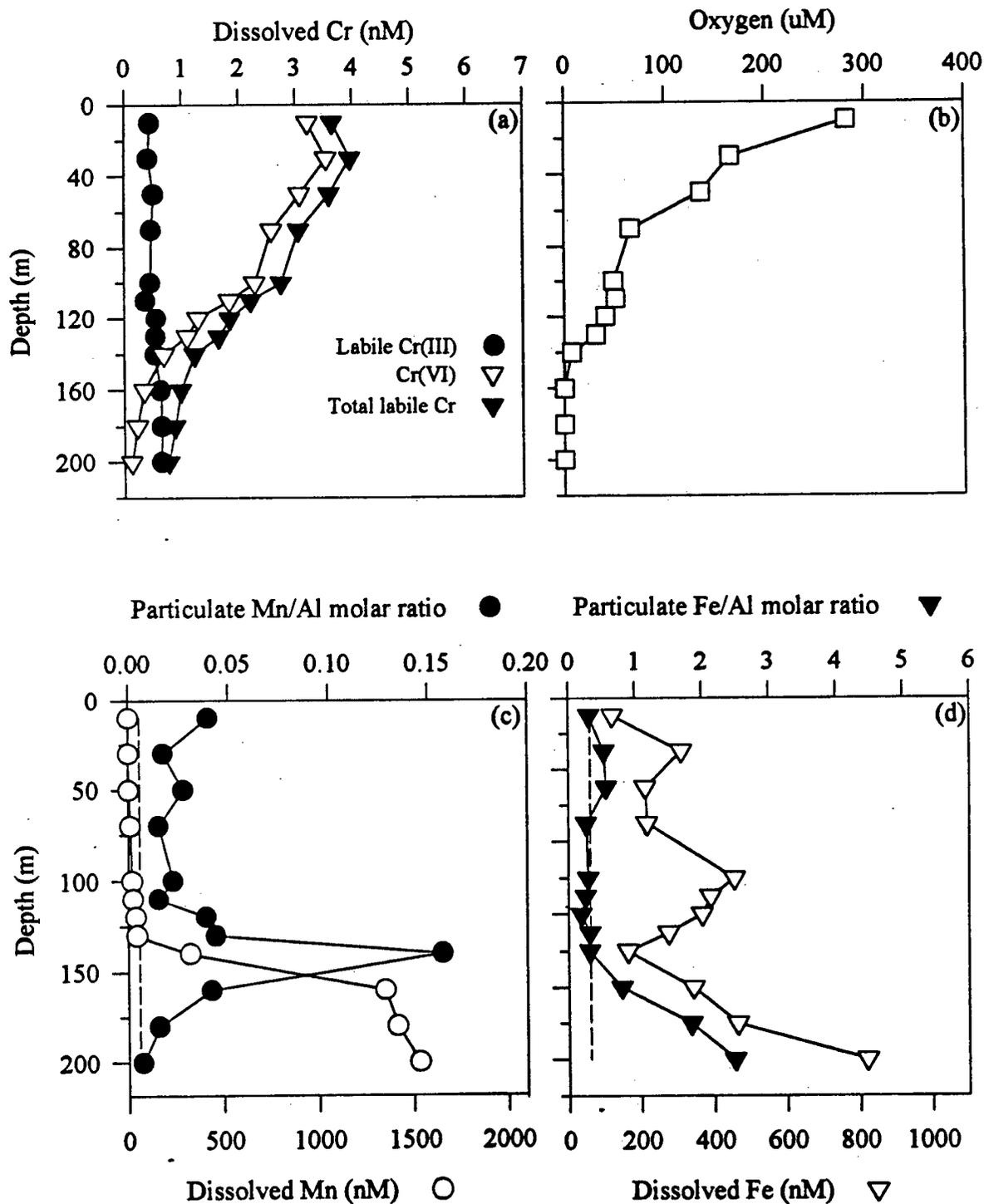


Figure 4.21: Saanich Inlet data for JULY 1995: (a) Chromium species (b) Dissolved Oxygen (c) Dissolved and Particulate Mn/Al molar ratio (d) Dissolved and particulate Fe/Al molar ratio. Dashed lines in (c) & (d) represent crustal metal/Al molar ratio.

4.3.3 CHROMIUM

4.3.3.1 Time-Depth Distribution

The time-depth distribution of total labile Cr during the annual cycle is shown in Figure 4.3 with individual monthly data presented in Figures 4.9-4.21. Total labile Cr values range from 7.2 nM at the surface to 0.74 nM in the bottom. Cr(VI) values vary from 5.9 nM to 0.10 nM whereas labile Cr(III) concentrations are lower (0.20-1.7 nM) but much higher than expected from thermodynamic calculations (Chapter 1). Cr(VI) is the dominant Cr species in the oxic zone throughout the annual cycle as expected. Labile Cr(III) predominates in the anoxic zone only during stratification (May-July 1994 and March-July 1995). Higher values for total labile Cr and Cr(VI) at the surface in fall and spring likely results from increased supply through riverine discharge as well as from snow melts during these periods.

4.3.3.2 The Cr Annual Cycle in Saanich Inlet

The chromium cycle in Saanich Inlet shows variations that correlate with the changing water column redox conditions and the resulting Cr speciation transformations. In early winter (January) the waters were well mixed and total labile Cr ranged from 4.4 nM at the surface to 3.4 nM at 200 m. Cr(VI) was the dominant Cr species; labile Cr(III) made up between 15 % to 20 % of the total labile Cr and non-labile Cr forms were not detected. By February, when the oxygen values in the bottom waters have started to drop, total labile Cr decreases from 3.5 nM at the surface to 2.1 nM at 200 m. Cr(VI) is still the dominant Cr species throughout the water column with labile Cr(III) contributing as much as 40 % of the total labile Cr at 200 m; the non-labile Cr contribution was not determined.

By March and April, with increased water column stratification, labile Cr(III) is now the dominant Cr form in the deep waters, accounting for greater than 90 % of the total labile Cr in the deepest samples. The contribution of non-labile Cr to the total is, however, still negligible. Between May and July, anoxia at depth increased and H₂S was detected in the bottom samples. It was only during this period that non-labile Cr was detected in the bottom samples in June

(160 m) and in July (140-200 m). The non-labile Cr fraction made up between 45 and 55 % of total oxidizable Cr in July 1994. Labile or "free" Cr(III) comprised between 20 and 35 %, with Cr(VI) accounting for 10-35 % of total detectable Cr. A net loss of Cr in the bottom waters is also seen during this period, presumably due to sorption and/or coprecipitation of Cr(III) with subsequent removal. In their study of Cr cycling in Greifensee lake, Switzerland, Johnson *et al.* (1992) found that under reducing conditions, approximately 20 % of the Cr remained unreduced as Cr(VI) even in the presence of S(-II). Approximately 15 % of the Cr detected was free Cr(III) with the remainder being colloidal Cr. It appears, therefore, that Cr speciation and cycling in Saanich Inlet and Greifensee lake may be controlled by similar factors.

The deepening of the interface to 160 m in August marked the start of deep water renewal in the Inlet. Cr(VI) was now the dominant Cr species in the deeper samples below 160 m. This likely results from a combination of advected dense, oxygenated waters with higher Cr concentrations flowing in over the sill and *in situ* oxidation of non-labile Cr forms present. The relative magnitude of the contribution from each source, however, cannot be presently assessed as non-labile Cr forms were not determined. In addition, deep water renewal estimates are reported to be variable from year to year, ranging from 18 to 46 % (Anderson and Devol, 1973). In September and October, as a result of the flushing cycle and upward migration of the redox interface, higher total labile Cr and Cr(VI) values were seen above and below the interface. The increase in Cr in the bottom waters is quite dramatic; from < 1 nM Cr(VI) in August to > 2 nM Cr(VI) in September and October (more than 150 % increase). Once again Cr(VI) was now the dominant Cr species in the entire water column.

4.3.3.3 Geochemical Factors Controlling the Cr Cycle

Field observations in Saanich Inlet show that Cr(VI) is stable in oxic and intermediate redox water conditions (5-20 $\mu\text{M O}_2$). With increased anoxia in bottom waters, net Cr removal is observed. As chromate is the dominant Cr species in the oxic region, the observed loss of Cr implies either loss of Cr(VI) directly or after reduction to Cr(III). The negatively charged Cr(VI) anions are repelled by similar charges on the oxide surfaces of particulates in neutral to basic waters and Cr(VI) is therefore not expected to undergo direct sorption to particles.

Thermodynamic calculations can be used to assess the likely reductants (Froelich *et al.*, 1979). Reduced species of redox couples with pE values lower than Cr are candidates. Of these, Fe(II), S(-II) and organic compounds, the latter possibly by microbial mediation, have been found to act as reductants for Cr(VI) (Schroeder and Lee, 1975) and are all present in the inlet during stratification. H_2S was only detected by smell from May 1994-July 1994 and in July 1995 but may have been present in concentrations too low to be detected by smell in March and April. Further insight into Cr transformation processes was made possible through laboratory studies on samples collected from the field. The results of these experiments (discussed fully in Chapter 6) support field observations that processes such as Cr(VI) reduction, Cr(III) binding by DOM and sorption to particles are important controls in regulating the distribution of Cr species in aquatic environments.

The determination of "total oxidizable Cr" was conducted on only a few samples as few of the field samples remained by the time this analytical step was optimized, approximately one year after the study began. Oxidation with hydrogen peroxide and irradiation with UV light revealed a portion of Cr not previously detected in some of the deeper samples. The presence of non-labile Cr during the stratified summer months likely results from the tendency of Cr(III) to form complexes with organic and colloidal materials as was seen in laboratory experiments (Chapter 6). The existence of organic Cr species in seawater has been suggested in various studies (e.g. Nakayama *et al.*, 1981a; Ahern *et al.*, 1985; Kieber *et al.*, 1992) although their contribution to overall Cr aquatic geochemistry is not well understood. Using the iron coprecipitation technique

for Cr preconcentration, Emerson *et al.* (1979) observed an increase of Cr(III) and total labile Cr in the anoxic Saanich Inlet zone in July 1977. This method is, however, non-specific and detects colloidal and organic Cr forms present in the sample in addition to inorganic Cr(III) and some of the Cr(VI) (Osaki *et al.*, 1983). When the colloidal/organic Cr fraction in the Saanich summer results are considered, the detectable Cr increases, but not to the levels in upper oxic waters. These results are also consistent with similar findings by Johnson *et al.* (1992) in Greifensee lake, Switzerland, where colloidal Cr made up more than 50 % of the Cr in the deep waters before the lake turnover occurred. They are also in agreement with the results of Balistrieri *et al.* (1992b) who observed a net loss of Cr during sub-oxic and anoxic conditions in Lake Sammamish, Washington.

4.3.3.4 Labile Versus Non-labile Cr

The Saanich inlet results indicate that a fraction of the Cr in the deep waters during stratification is not labile enough to be detected by ECD-GC without further sample processing. On sample oxidation with $\text{H}_2\text{O}_2/\text{UV}$ light, the ECD-GC detected Cr increases by as much as 100 %. As chromium samples were not filtered prior to analysis, it is possible that the Cr increase in oxidized samples may also result from leaching of Cr in suspended particles. Direct particulate Cr measurements in these samples were not undertaken due to blank problems. The acid-washed polycarbonate filters, which had low Mn, Fe and Al blank levels, suffered from unacceptably high Cr blanks, most likely produced during the fabrication process. However, particulate Cr likely requires more vigorous digestion with concentrated mineral acids as does particulate Mn, Fe and Al; one may therefore be justified in using the total oxidizable ($\text{H}_2\text{O}_2/\text{UV}$) Cr value to estimate fractions of labile, non-labile and scavenged Cr during stratification. If one takes an average value of 3.5 nM as being representative of the water column concentration during the summer season, one finds that approximately 10 % (0.34 nM) of Cr in deep waters is free or "labile" Cr(III), ~ 10 % (0.36 nM) exists as Cr(VI), about 30 % (1.1 nM) is "non-labile" and approximately 50 % (1.7 nM) is removed from the system in deep waters presumably via scavenging onto particles. Based on both field observations and laboratory studies, it can thus be proposed that the principal geochemical control on Cr concentration and distribution in Saanich Inlet is reduction of most of the Cr(VI) to Cr(III) under suboxic and anoxic conditions. About half of the reduced Cr is detectable by the ECD-GC in the deep waters as either "free" or "bound" Cr; the rest appears to be scavenged and removed to the sediments.

4.3.4 MANGANESE, IRON and ALUMINUM

4.3.4.1 Redox Cycling of Mn and Fe

The distribution of Fe and Mn in aquatic systems is controlled by the chemical characteristics of the oxidation states of the two metals and the physical, chemical and biological characteristics of the environment. A thorough discussion of the behavior of these elements across redox gradients has been presented by, amongst others, Davison (1993); only the key features of the distribution will be summarized here.

Both Fe and Mn exist as insoluble metal oxyhydroxides in the higher oxidation states (Fe(III) and Mn(III/IV)). These oxyhydroxides have large adsorption capacities for cations and anions and, as a result, may control the concentrations of other ions. The reduced forms of both metals (Fe(II) and Mn(II)) tend to be soluble and mobile, unless the ion activity products of Fe or Mn and anions such as sulfide, carbonate or phosphate exceed the solubility products of the corresponding minerals. The two metals differ in their redox potentials and rates of oxidation. Mn oxides reduce at a higher potential than Fe oxide and, although both of their oxidation rates are strongly dependent on pH, Fe oxidizes much more rapidly than Mn. These differences in redox potential and oxidation rates can result in temporal and spatial differences in concentration profiles.

The distribution of Fe and Mn in Saanich Inlet is examined in light of these chemical characteristics as well as the biochemical and physical processes occurring in the inlet. The discussion addresses specifically cycling across redox boundaries in the water column and sediments as a result of stagnation and oxygen utilization, followed by deep water renewal.

4.3.4.2 Time-Depth Distribution of Mn

The yearly cycles of dissolved and particulate Mn are presented as time-depth-concentration contours in Figures 4.4 and 4.5, respectively and as monthly data sets in Figures 4.9-4.21. Dissolved Mn is low in the upper oxic waters (< 100 nM) throughout the cycle. Concentrations in the deep waters vary with season and range from 31 nM to 1990 nM with the highest values during the stratified summer months. Particulate Mn values are lower than dissolved Mn values with a maximum of 115 nM at 200 m in November 1994. The distribution of particulate Mn shows that the highest values occur at mid-depth during the stratified summer months and in the bottom waters following overturn.

4.3.4.3 Time-Depth Distribution of Fe

The time-depth distribution of dissolved and particulate Fe during the annual cycle are shown in Figures 4.6 and 4.7, respectively. Monthly concentration-depth profiles are presented in Figures 4.9-4.21. The concentrations of dissolved Fe (11-1000 nM) are generally lower than dissolved manganese. Dissolved Fe increases in the bottom waters during spring and summer. Particulate Fe, unlike particulate Mn, increases in the bottom waters during the spring and summer when H_2S is detectable. Large particulate Fe signals in the fall and spring at the surface and mid-depth reflect detrital inputs probably through river runoff and snow melts during these periods.

4.3.4.4 Dissolved Mn and Fe Cycles

Profiles of dissolved Mn and Fe through the yearly cycle show changes with time in response to changing water column redox conditions. Dissolved Mn concentrations in the bottom waters in winter and spring show an increase from mid-depth towards the bottom. The linear to concave shape of these profiles in the bottom waters suggests that the dominant source for dissolved Mn is most likely the reduction of oxyhydroxides in the sediments and diffusion to the overlying water column (Davison, 1985). Dissolved Fe concentrations, on the other hand, are

low in bottom waters. This suggests either that the sediments are not a source of Fe(II) or that the much faster Fe(II) oxidation rate results in the low observed dissolved Fe concentrations. Release of Fe(II) from sediments in lake systems with seasonal anoxic conditions is similarly less marked than the release of Mn(II) (Davison, 1993). The oxidized Fe must be rapidly returned to the sediments as particulate iron concentrations in bottom waters are low during this period. It is only in spring with low bottom water dissolved oxygen levels (5-10 μM) that dissolved Fe increases near the sediment-water interface, going from 310 nM in February to 840 nM in April at 200 m. The bottom water concave-shaped profile suggests that the sediments are likely the major source of Fe(II) to the deep waters.

With increased anoxia during the summer months, the bottom water dissolved Mn profiles change to display smooth convex shapes with broad maxima below the redox interface. The dissolved Fe profiles also show changes with a less pronounced convex-shaped profile in bottom waters during the same period. These changes suggest that reduction of metal oxides associated with settling particles within the water column may now be the predominant source of dissolved metal concentrations.

In August the influx of new, dense oxygenated waters into the inlet results in oxidation of reduced species and a decrease in Mn(II) concentration in the bottom waters. Bottom water dissolved Fe concentrations, however, increases over the July values. This is consistent with dissolved Fe(II) control by soluble Fe(II) (poly)sulfide phases. The oxidation of these sulfides to sulfates will result in increased Fe(II) concentrations until the formation of insoluble Fe oxyhydroxides limits dissolved Fe concentrations. Advection of new, dense oxygenated water into the bottom of the inlet in September and October results in an upward displacement of the reducing water mass, which results in a mid-depth zone between 100 and 140 m that is more reducing than the regions above and below it. Dissolved Mn and Fe values therefore both show higher values in this mid-depth region. Increased mixing in late fall leads to detection of dissolved oxygen all the way to the bottom of the inlet; dissolved Mn in bottom waters decrease from the highest observed values in summer (maximum ~ 2000 nM) to ~ 40 nM in November as Mn(II) is

oxidized to particulate Mn. After this, the redox boundary once again shifts to the sediments. Thus gradual changes in the redox conditions with depth and time and differences in the redox potentials of Fe and Mn result in quite different shapes for the dissolved profiles of the metals at any given time.

4.3.4.5 Particulate Al

Aluminum forms 8.2 % of the earth's crust and is therefore a major component of detrital material. It is therefore important to monitor the concentration of particulate Al alongside those of the other trace elements in order to assess the detrital contribution to the measured particulate value. Particulate Al concentrations ranged from 16-5150 nM during the annual cycle (Figure 4.8). The highest particulate Al concentration observed (5150 nM) was in November near the sill depth, which also corresponded to the highest particulate Fe concentration (2280 nM) detected during the cycle. Thus these signals likely result from detrital inputs through rivers that drain into the inlet (Figure 4.1) which are at their maximum during the rainy fall months. The particulate Al peak, like the particulate Fe peak, decreases in subsequent months presumably through sinking and dissolution of particles as stratification is established in the water column. The lowest particulate Al concentrations at mid-depth are observed in May 1995 (172 nM).

4.3.4.6 Particulate Mn and Fe

The particulate Mn and Fe profiles, like the dissolved profiles, also show changes with changing water column redox conditions. In the stratified summer months, particulate Mn is a sharp peak above the interface with lower concentrations both above and below this peak. This Mn peak results from diffusion of Mn(II) from the sub-oxic zone into the oxic zone where it is unstable and is oxidized. The cycle of reductive dissolution and oxidation/precipitation results in the formation of the particulate Mn peak above the dissolved maxima, a feature commonly observed in similar environments (e.g., Spencer *et al.*, 1972; De Vitre *et al.*, 1988; Landing *et al.*, 1991). The oxidation process is bacterially mediated (Emerson *et al.*, 1982). In contrast, particulate Fe shows increases with depth in the anoxic zone during advanced stratification with no mid-depth maxima. The lack of a pronounced particulate Fe peak above the interface was also seen in the Black Sea by Spencer *et al.* (1972) and Lewis and Landing (1991). The latter authors suggested that a short residence time before dissolution for the particulate Fe-oxyhydroxides formed from oxidation of diffusing Fe(II) was a likely explanation for the lack of a particulate Fe maximum. When the particulate Mn and Fe concentrations are normalized to particulate Al, these trends are clearer: the enrichment of Mn in the suboxic zone is evident as well as Fe enrichment in the anoxic region due to the formation of Fe-sulfide phases.

Comparison of deep water particulate, dissolved, and total Mn and Fe concentrations illustrates the unique phase transitions that take place across the interface during stratification. Whereas Mn is present mainly in dissolved form and particulate Mn is low (< 5 nM), dissolved iron levels are comparable to particulate levels. Iron undergoes two phase transitions as waters become more reducing. In oxic waters, iron is present mainly in particulate form because Fe(III) is extremely insoluble. In reducing environments iron oxyhydroxides undergo reductive dissolution and dissolved Fe(II) becomes predominant. When sulfide concentrations become high, the formation of insoluble iron sulfides takes precedence and drives the Fe(II) back into particulate form. Thermodynamic calculations (Jacobs and Emerson, 1982) show that iron solubility in the anoxic Saanich Inlet zone is likely controlled by greigite (Fe₃S₄) whereas this

zone is undersaturated with respect to alabandite (MnS), haurite (MnS₂) and also rhodochrosite (MnCO₃).

In fall, oxygenation of previously anoxic bottom waters results in oxidation of reduced species. Particulate Mn concentrations increase in the bottom waters from oxidation of dissolved Mn previously present in the anoxic zone. The particulate Mn/Al ratios reveal enrichment in the bottom waters, confirming that the enhanced particulate Mn concentrations during this period results from *in situ* oxidation rather than an external source, brought in with the advected water. Non-equilibrium conditions exist in September and October where substantial concentrations of both reduced manganese and iron are observed in the presence of oxygen. Particulate Mn shows the largest increase in bottom waters between September and November. Particulate Fe is low in the bottom waters in fall with peak values at mid-depth (110-140 m) in September. The particulate Fe/Al profiles show an enrichment of Fe at mid-depth with ratios approaching crustal values in the bottom waters. The origin of this mid-depth enrichment is not clear; it could result from horizontal transport processes from shallow sediments. It may also be due to particulate iron formed via oxidation of Fe(II) in deep waters during overturn transported to mid-depth with the upward movement of the interface.

Particulate Mn concentrations decrease in bottom waters due to reduction of Mn oxyhydroxides in winter and spring as oxygen concentrations decrease and waters become more reducing. As stratification begins to be established once again, a redox boundary ensues at mid-depth and Mn cycling in the water column results in a particulate Mn peak which intensifies with time. Particulate iron continues to be low in the bottom waters in winter with increases occurring in the spring. This increase coincides with increases in dissolved Fe in the bottom waters and likely results from oxidation of some of the sediment derived Fe(II). As the bottom waters turn anoxic in summer, the particulate Mn and Fe profiles begin to resemble those seen the previous year.

4.3.5 Assessment of Cr Carrier Phases

Under oxic conditions, Mn and Fe oxyhydroxides, together with biogenic organic matter, are generally regarded as the most important scavenging or carrier phases for trace elements in aquatic environments (Hart, 1982; Forstner, 1982; Sigg, 1985; Tessier, 1992). Trace elements associated with metal oxyhydroxide phases should be released to the dissolved phase during reductive dissolution of the oxides under suboxic and anoxic conditions. Trace element-organic matter interactions can be via binding, sorption and complexation processes in the water column; subsequent degradation of organic matter at depth can lead to release of scavenged metals.

Association of Cr with Mn and Fe is made complex by the contrasting geochemistry between Cr and both Mn and Fe. In the oxic zone, chromium speciation is dominated by soluble, non-particle reactive Cr(VI) whereas Mn and Fe exist as insoluble oxyhydroxide particles. During stratification, dissolved Mn and Fe concentrations increase in the suboxic and anoxic regions from reductive dissolution of oxides. Labile Cr(III) is, however, low and more or less invariant with depth and total oxidizable Cr shows a slight increase in bottom waters. Thus Cr concentrations in Saanich Inlet deep waters may be regulated, in part, by the interaction of this element with organic matter via formation of organic/and or colloidal non-labile forms. Humic substances can sorb onto the surfaces of Mn and Fe oxides and in so doing may determine their surface characteristics as transport agents for other metals (Tipping and Heaton, 1983; Tipping and Ohnstad, 1984). It is likely therefore that the main Cr carrier phase in the Inlet is organic matter. This may also be sorbed onto the surface of Mn and Fe oxyhydroxides and released when these phases undergo reductive dissolution in the anoxic zone. Direct sorption of inorganic Cr(III) onto Mn oxides is, in addition, not a viable route as these oxides are reported to be the most important oxidants of Cr(III) in aquatic systems (Schroeder and Lee, 1975) and would therefore remobilize Cr as soluble Cr(VI). The surface characteristics of oxyhydroxides onto which humics are bound, coupled with the predominance of non-labile Cr forms may, however, be such that oxidation and remobilization of Cr may be inhibited. A similar effect was reported by

Johnson *et al.* (1991) who observed that Cr(III) bound by salicylic acid was less susceptible to oxidation by Mn oxides than unbound Cr.

Laxen (1984, 1985) and Laxen and Sholkovitz (1981) reported a series of laboratory sorption experiments with Fe oxides under lacustrine conditions in which sorption was modified substantially in the presence of humic substances. Cd and Ni sorption was enhanced in the presence of humics whereas Cu sorption decreased. This was attributed, respectively, to strong binding of Cd and Ni to sorbed humics (i.e., "ligand-like behavior") and the greater affinity of Cu to the dissolved humic fraction. Cr, like Cu, tends to form organic complexes with DOM (Osaki *et al.*, 1983; Douglas *et al.*, 1986). It is likely that direct chromium sorption to Mn and Fe oxides may also be similarly inhibited by complexation with organic matter.

Water column profiles of dissolved Cr concentrations in the aquatic environment which link Cr behavior directly to Fe and Mn oxides, are relatively scarce. Cr cycling with Mn and Fe oxides was suggested by Balistrieri *et al.* (1994) in Hall Lake, Washington although the analytical scheme used did not discriminate between the different Cr forms. The seawater samples had also been stored acidified and it is probable that non-labile Cr-organic forms initially present would have degraded to release inorganic Cr. Total dissolved chromium concentrations in samples from the Black Sea (Chapter 5) which had been stored acidified for several years also show increase with depth in the suboxic and anoxic zones with total dissolved Cr displaying good correlations with dissolved Mn. A possible explanation is the degradation of non-labile organic and/or colloidal Cr complexes initially sorbed on the oxyhydroxide surfaces during the prolonged storage under acidified conditions. This is discussed further in Chapter 5.

4.3.6 Summary and Conclusions

Chromium speciation and cycling in Saanich Inlet is driven by the interplay of its own redox chemistry and the gradual changes in the water column redox conditions. The predominant Cr species in Saanich Inlet during oxic and suboxic conditions is Cr(VI). The most important removal mechanism appears to be reduction under suboxic and anoxic conditions. Even with no measurable oxygen concentrations (and in the presence of H₂S) Cr(VI) is present, contributing ~ 10 % of total detected Cr. Labile Cr(III) is generally low throughout the water column making up approximately 10 % of total dissolved Cr during the stratified summer months. Non-labile Cr is detected only during advanced stratification periods, making up approximately 30 % of the Cr in bottom waters. Thus colloidal and/or organic Cr contribution to Cr speciation appear to be significant only under strongly reducing conditions when H₂S is detected. The Cr cycle in Saanich Inlet can thus be summarized: input of Cr occurs mainly as Cr(VI) and is therefore quite stable under oxic conditions. Removal via reduction and sorption of Cr(III) occurs in the anoxic deep waters with no apparent remobilization from the sediments to counterbalance the loss.

The results of the study of Mn and Fe cycling in Saanich Inlet reveal that the seasonal anoxic characteristics of this environment are responsible for significant water column changes in the concentration and speciation of both elements. During suboxic and anoxic conditions, large increases in dissolved Mn and Fe occur due to reductive dissolution of their insoluble oxyhydroxides. Fe solubility during the latter stages of stagnation appears to be controlled by authigenic sulfide mineral formation. Large increases in bottom water particulate Mn values occur in fall as a result of *in-situ* oxidation of dissolved Mn previously present. A shift in the Mn redox boundary between sediments and the water column is seen between fall and winter as dissolved oxygen in deep waters is used up. Loss of iron in bottom waters occurs in fall as a result of oxidation of sulfide phases with subsequent precipitation and removal of oxyhydroxides. Detrital inputs of Fe and Al in fall and spring through precipitation and river run-off result in elevated concentrations of these elements near the surface and at mid-depth during these periods. The results of this study confirm that transformations of Mn and Fe between dissolved and

particulate phases across redox boundaries in the inlet have the potential to influence the behavior of other trace elements through sorption, coprecipitation and reductive dissolution. The main Cr carrier phase appears to be biogenic organic matter onto which Fe and Mn oxyhydroxides may also be sorbed at the interface and released when these phases undergo reductive dissolution.

Chapter 5

Section I: Geochemical Cycling of Chromium in the Black Sea

5.1 INTRODUCTION

The cycling of metals that occurs across the redox interface in the water column and sediments has received a lot of attention over the last two decades. Understanding the processes occurring in these interface zones can provide insight into the redox cycling of metals in a variety of other environments where redox gradients occur such as oxygen-minimum zones, microenvironments and hydrothermal vent areas. Anoxic fjords, where an oxic/anoxic interface develops in the water column, have been used as model systems for studying the factors controlling the solubility of trace metals in oxygenated and anoxic waters (Emerson *et al.*, 1983; Jacobs and Emerson, 1982; Landing and Westerlund, 1988); and to study the partitioning and transport of trace metals across redox boundaries (Jacobs *et al.*, 1985; Mugo, 1997-this thesis, Chapter 4). They have also been used to study the kinetics of oxidation and reduction of redox sensitive metals (Emerson *et al.*, 1979; Emerson *et al.*, 1982; Tebo and Emerson, 1986) and to assess the role of bacterial catalysis of metal redox reactions (Emerson *et al.*, 1982; Rosson *et al.*, 1984; Tebo and Emerson, 1985; Tebo *et al.*, 1984).

The Black Sea is the world's largest permanently anoxic basin (508,000 km²) and is thought to provide a quasi-steady state system. It is anoxic because of its strong vertical salinity stratification (Caspers, 1957; Sorokin, 1983) caused by excess of precipitation and river run-off over evaporation (Tolmazin, 1985a). The deep water has a higher salinity due to the inflow of Mediterranean water which enters through the Bosphorous Strait (Figure 5.1.1). The depth of the halocline in the Black Sea reflects a balance between freshwater and seawater inflows. This density gradient inhibits mixing and is the origin of the stability of the oxic-anoxic interface.

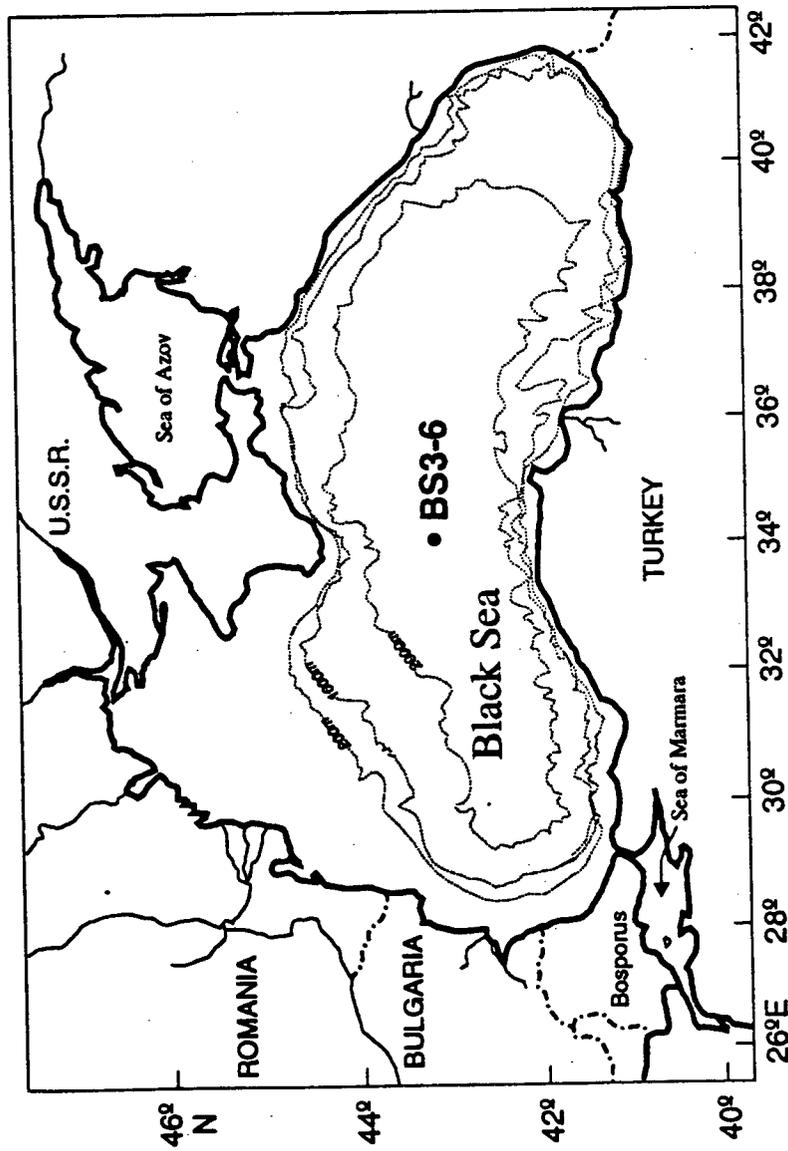


Figure 5.1.1 Area map of the Black Sea showing the location of station BS3-6. Samples collected in July 1988 were supplied by W. M. Landing from Florida State University (FSU).

The Black Sea is a superior environment for investigating the processes that occur in anoxic waters and at the boundaries of oxic/anoxic interfaces because of the relative stability of the anoxic zone and a fairly broad oxic/anoxic interface that tends to separate the various processes. In spite of its importance, the Black Sea was until recently relatively unexplored as a study site for trace element geochemistry. Some of the earliest reported studies on trace metal geochemical behavior in the basin include the description of the manganese cycle across the redox interface (Spencer and Brewer, 1971) and a discussion of the distribution of various trace metals in suspended matter (Spencer *et al.*, 1972).

It is, however, mainly as a result of the 1988 US-Turkish Black Sea Expedition that our understanding of the marine chemistry of this basin has improved tremendously. Using a variety of modern sampling and analytical techniques, a comprehensive study of the Black Sea, covering not only trace metals, but also hydrography, nutrients, the organic carbon cycle and benthic processes, was conducted. The results were published in a special edition of *Deep-Sea Research* (Murray, 1991). Lewis and Landing (1991) presented a detailed study of the distribution and speciation of manganese and iron whereas Tebo (1991) discussed studies of the microbially catalyzed manganese(II) removal and oxidation rates. The cycling of manganese across the interface was shown to influence the distributions of rare earth elements (REE) (Schijf *et al.*, 1991) and also ^{234}Th (Wei and Murray, 1991).

The present study seeks to extend our understanding of trace metal geochemistry in the basin by determining the distribution of dissolved chromium in the water column. Chromium exists in nature in two oxidation states. Thermodynamic calculations predict that in oxygenated waters, Cr(VI) as CrO_4^{2-} should dominate. In anoxic conditions, Cr(III) as mostly $\text{Cr}(\text{OH})_2^+$ is favored. Chromium distribution in the Black Sea should therefore mainly reflect processes related to its redox-chemistry and the expected speciation changes across the redox boundary coupled, perhaps, with the redox cycles of Mn and Fe. This is the first water column Cr data reported from this basin.

5.2 MATERIALS AND METHODS

5.2.1 Sample Processing and Analysis

Seawater samples for trace metal analyses collected during Leg III of the 1988 Black Sea Expedition were supplied by W. M. Landing from Florida State University (FSU). Samples were collected at Station BS3-6 (Figure 5.1.1) using a rosette/bottle system and also from a submersible pump sampling system. The sampling bottles were 28.5 L, Teflon[®]-coated, ball-valve PVC bottles constructed at the University of Washington, Seattle, WA. Samples were pressure filtered (N_2) in a make-shift trace-metal clean area in the ship, through acid-washed, pre-weighed 142 mm, 0.4 μm Nuclepore filters held in Teflon[®] filter sandwiches. The filtered samples were collected in acid-washed, 4-L polyethylene bottles and acidified to pH \sim 2 with Q-HCl (Lewis and Landing, 1991).

Sample processing and analysis for dissolved and particulate Mn and Fe by GFAAS, as well as detailed discussion of the results, have been presented elsewhere (Lewis and Landing, 1991). Only total labile Cr can be determined on these stored acidified samples. This was accomplished by the use of the electron capture detector gas chromatographic (ECD-GC) technique described fully elsewhere (Mugo and Orians, 1993). This method involves chelation of total labile Cr as Cr(III) by 1,1,1-trifluoro-2,4-pentanedione (Htfa) and extraction into 1 mL of toluene. Cr(VI) is reduced to labile Cr(III) within 24 hrs in acidified samples (Campbell and Yeats, 1981). Chromium is analyzed in the extracts by injection into the GC.

5.3 RESULTS AND DISCUSSION

5.3.1 Chromium Distribution

The total dissolved Cr concentration at station BS3-6 is plotted as a function of depth in Figure 5.3.1.1. Total Cr shows high values (2.2-2.6 nM) in the oxic waters, which decrease to a minimum of 1.6 nM at the top of the oxic-suboxic zone (80 m). Concentrations then increase with depth in the suboxic and anoxic zones with a value of 2.3 nM at the interface between the suboxic and anoxic zones. The highest value (2.9 nM) was detected at 250 m in the sulfidic, anoxic waters.

5.3.2 Redox Cycling

The distribution of chromium in the Black Sea is driven by a combination of its own redox chemistry plus a possible association with the redox cycles of Mn and Fe, which are ubiquitous in most aquatic environments. Chromium geochemical behavior is influenced by the existence of chromium in two oxidation states with vastly different properties. The samples analyzed in this study were acidified after collection and therefore only total labile Cr could be determined. The decrease in total labile Cr at the oxic-suboxic interface most likely results from removal of Cr(III) after reduction of Cr(VI). Loss of Cr(VI) directly via sorption is not expected as Cr(VI) is soluble and not attracted to particles.

The reduced Cr(III) (as $\text{Cr}(\text{OH})_3^0$ or $\text{Cr}(\text{OH})_2^+$) is particle reactive and is removed at the interface via sorption to particle surfaces. The increase in total labile Cr with depth through the suboxic and anoxic regions likely results from release when the particles undergo dissolution and/or reduction. In addition, reduced Cr(III) can be stabilized in the anoxic zone via interactions with organic matter and/or colloids, allowing it to remain in solution.

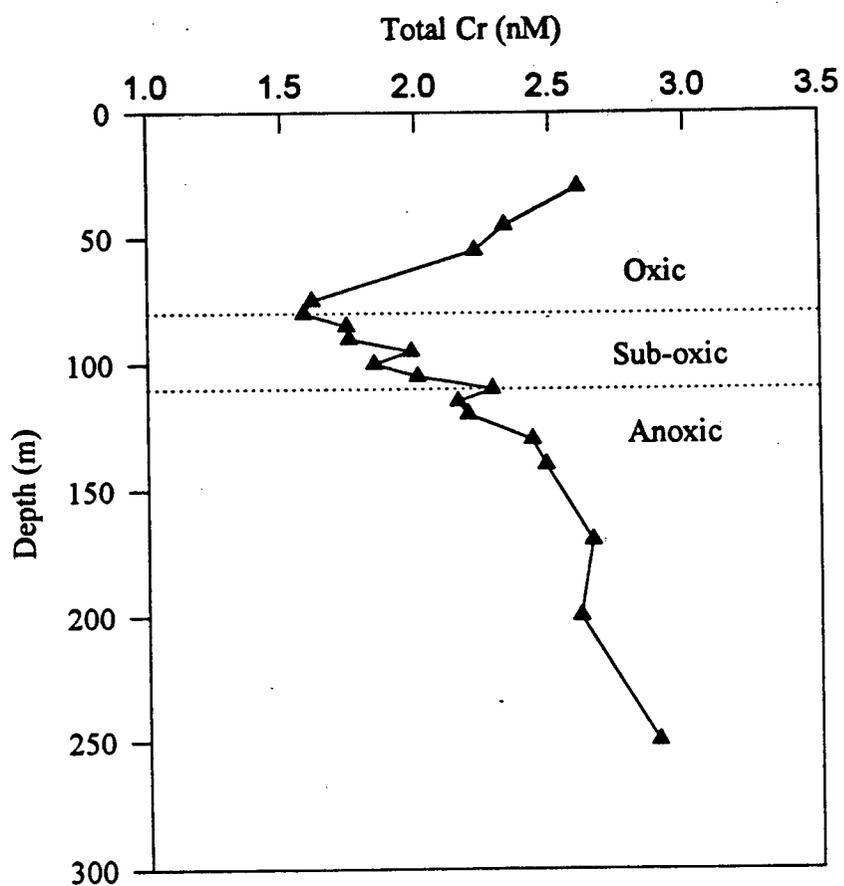


Figure 5.3.1.1 Total dissolved Cr data for Station BS3-6 in the Black Sea

5.3.3 Processes Affecting the Chromium Cycle

The distribution of dissolved and particulate Mn and Fe at station BS3-6 (Lewis and Landing, 1991) are shown in Figure 5.3.3.1. In oxygenated waters, Mn and Fe exist as insoluble oxyhydroxides (Mn(III, IV) and Fe(III)) which can scavenge other labile trace elements. Under reducing conditions, the oxyhydroxides undergo reductive dissolution to the soluble Mn(II) and Fe(II) cations; trace elements associated with the oxides should therefore be released under reducing conditions.

Both dissolved Mn and Fe show large increases in the sub-oxic and anoxic regions of the Black Sea. The distribution of total dissolved Cr, like that of dissolved Mn, shows a steep gradient across the oxic-suboxic interface. The particulate Mn profile shows a two peak maxima situated at ~ 75 m and 105 m, with the larger of the two at approximately the same depth as the dissolved Cr minimum. Particulate Fe does not show a maxima above the dissolved profile which has been attributed to a possibly short residence time at the interface before dissolution (Lewis and Landing, 1991). Plots of total dissolved Cr versus dissolved Mn and Fe concentrations in the suboxic and anoxic regions reveal good correlations ($r^2 = 0.87$ for Mn vs. Cr and $r^2 = 0.60$ for Fe vs. Cr), suggesting that the Cr cycle may be associated with the cycles of manganese and Fe. The distribution of other trace elements in the Black Sea, e.g. the rare earth elements (REE), has also been shown to be influenced by the Mn cycle (Schijf *et al.*, 1991).

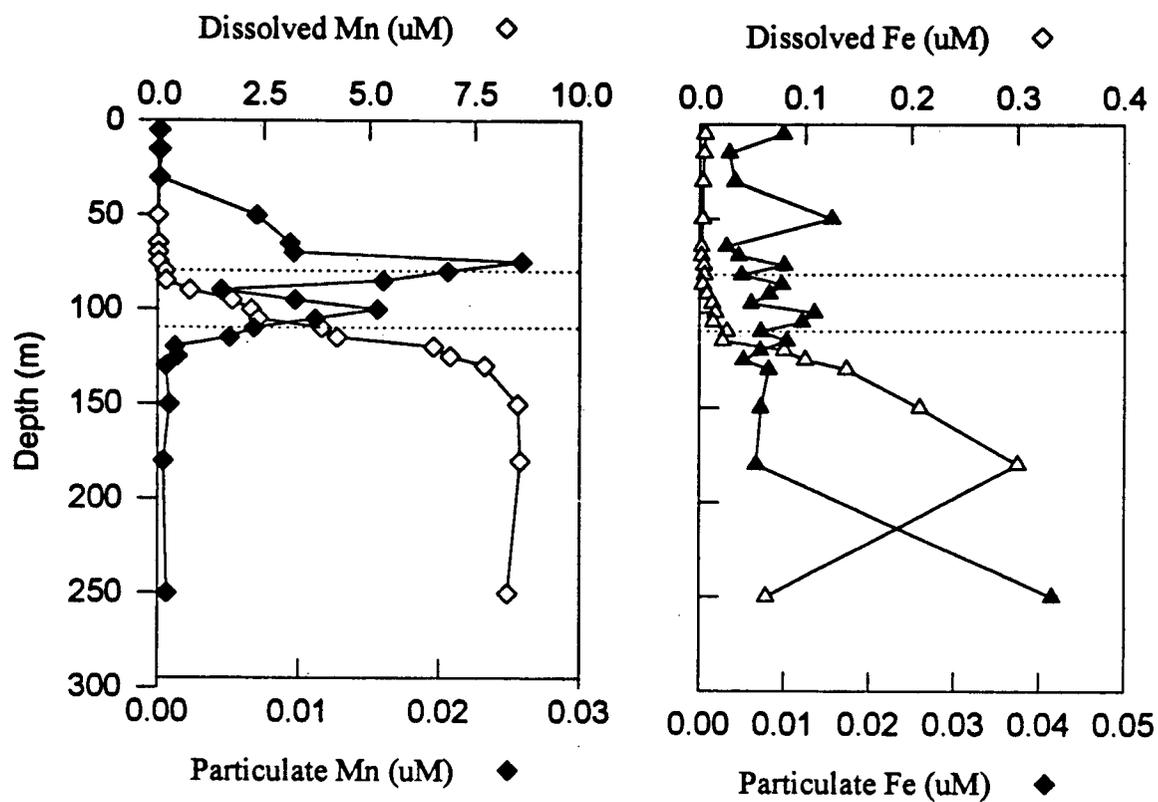


Figure 5.3.3.1 Dissolved and particulate Mn and Fe distributions at station BS3-6 (from Lewis and Landing, 1991)

Experimental evidence shows that Mn oxidation in the Black Sea is bacterially mediated (Tebo, 1991). The two particulate Mn maxima, one of which is located near the dissolved Cr peak minimum, are coincident with maxima in the ^{54}Mn uptake rate (Tebo, 1991), supporting an increase in the activity of Mn-oxidizing bacteria at these depths. Microbial reduction of Cr(VI) has also been demonstrated in various environments (see Turick *et al.*, 1996 and references contained therein). Thus it is likely that Cr(VI) reduction at the Black Sea interface is via a microbially mediated pathway in a similar manner to Mn oxidation, although a purely abiotic process with Fe(II) or S(-II) cannot be ruled out. As hydrogen sulfide is not detectable at the dissolved Cr minima, and Fe(II) concentrations are quite low, the purely abiotic reduction of Cr(VI) by these reductants, if occurring, would likely take place within a reduced microniche environment at the interface as discussed by Jorgensen (1977). The reduced Cr is likely sorbed onto sinking (bacterial) particles onto which Mn and Fe oxides are associated. Reductive dissolution of the oxides and/or dissolution of the particles in the anoxic zone results in release of sorbed Cr(III).

Because of the tendency of Cr(III) to form complexes with organic materials and colloids (Osaki *et al.*, 1983; Douglas *et al.*, 1986), this species may exist complexed or bound by colloids in the anoxic Black Sea waters. These seawater samples were stored acidified at $\text{pH} < 2$ for almost 8 years prior to analysis. In addition to reduction of Cr(VI) to Cr(III), organic chromium complexes in the samples would likely have degraded to release Cr(III) after the long storage period. Organic Cr complexes have been shown to be easily degradable with significant degradation occurring even on exposure to ambient sunlight (Kaczynski and Kieber, 1994). This was tested by oxidative digestion ($\text{H}_2\text{O}_2/\text{UV}$ light) of several samples from the anoxic zone. The results indicated no additional release of Cr from these samples confirming that any colloidal and/or organic Cr forms initially present had degraded during storage. Prolonged storage of acidified seawater samples from the Mediterranean was similarly found to cause an increase in

detected Al and Ti which was attributed to release of inorganic colloidal and organic complexes of these elements (van den Berg *et al.*, 1994).

5.3.4 Comparison With Saanich Inlet Data

The distribution of chromium species, Mn and Fe during the stratified summer season (July 1994) in Saanich Inlet, an intermittently anoxic fjord, are shown in Figure 5.3.4.1 (discussed fully in Chapter 4). The manganese and iron profiles in Saanich inlet are quite similar to those seen in the Black Sea. Dissolved metal concentrations increase in the suboxic and anoxic waters with particulate Mn showing a peak above the interface and particulate iron increasing with depth in the anoxic waters. These results suggest that the distributions of Mn and Fe in the two environments are likely controlled by similar geochemical factors.

Total dissolved Cr in oxic Saanich waters decreases to a minimum at the oxic-anoxic interface. The Cr minimum occurs at approximately the same depth as the particulate Mn maximum, similar to the situation in the Black Sea. However, it is only when the non-labile Cr fraction (Cr detected only after sample oxidation with hydrogen peroxide and irradiation with UV light) is considered that an increase in Cr is seen in Saanich Inlet bottom waters similar to the Black Sea. Unlike the Black Sea samples, Saanich Inlet samples were not acidified before analysis in order to preserve Cr speciation.

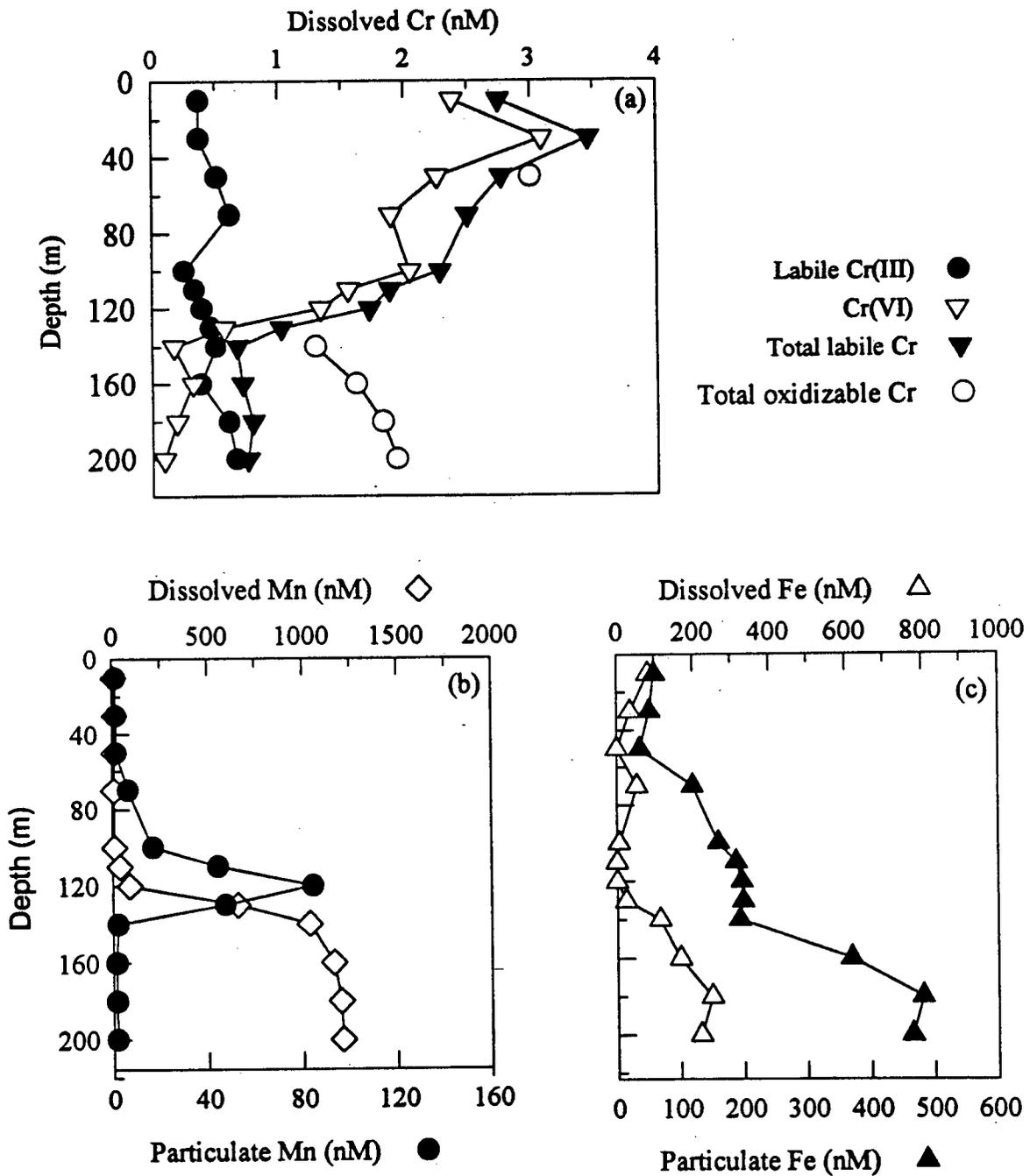


Figure 5.3.4.1 Saanich Inlet data for July 1994

(a) Chromium species (b) Dissolved and Particulate Mn
(d) Dissolved and particulate Fe

Comparing Saanich Inlet data and the Black Sea results, one concludes that reduction of Cr(VI) to Cr(III) at a redox interface results in the formation of mostly non-labile colloidal and/or organic Cr forms. These non-labile Cr forms are likely transported in association with the surrounding Mn and Fe oxyhydroxide coatings and are released in the anoxic waters during reductive dissolution of these phases. They appear to be quite stable under reducing conditions but can be degraded to release inorganic Cr either by prolonged storage in acidified conditions or by digestive oxidation with H_2O_2 /UV light. Note also that total Cr in Saanich Inlet deep waters even after digestive oxidation of samples is lower than in the oxic region. On the other hand, concentrations in anoxic waters of the Black Sea are approximately the same as the oxic region. Thus a net removal of Cr occurs in Saanich deep waters during stratification which does not appear to be the case in the Black Sea.

5.3.5 Modeling the Cr Cycle

The dissolved Cr cycle across the Black Sea interface can be fitted into a simple model combining vertical transport and *in situ* redox and removal processes (e.g. Cranston, 1979). The general equation defining diffusion and reaction processes for a one-dimensional vertical case is:

$$\partial[C]/\partial t = K_z (\partial^2[C]/\partial z^2) + J \quad \text{Equation 1}$$

where K_z is the vertical eddy diffusivity, t is time, $[C]$ is the concentration, z is the depth and J is the reaction rate term. Chromium data in the Black Sea show a minimum at the redox interface and higher values both above and below the interface. The main processes controlling Cr distribution are redox cycling between Cr(VI) and Cr(III) at the interface coupled with removal via sorption and/or coprecipitation. The Cr reaction rate term J can be, as a first approximation, represented by a pseudo-first order removal rate constant, k_r , incorporating both redox and sorption processes (e.g. Emerson *et al.*, 1979). In order to apply the model, conservative tracers such as salinity and temperature must be linearly related, as this represents a conservative mixing zone (no horizontal effects). The potential temperature-salinity profile for station BS3-6 (Figure 5.3.5.1) is linear over the region between 40 and 250 m.

Two other assumptions are made in solving the diffusion and reaction equation. First, steady state conditions are assumed, i.e., $\partial[C]/\partial t = 0$. This assumption is supported by the fact that dissolved and particulate Mn and Fe profiles determined during the 1988 cruise by Lewis and Landing (1991) are very similar to ones obtained almost twenty years earlier by Spencer and Brewer (1971). Second, the eddy diffusion coefficient, K_z , is assumed to

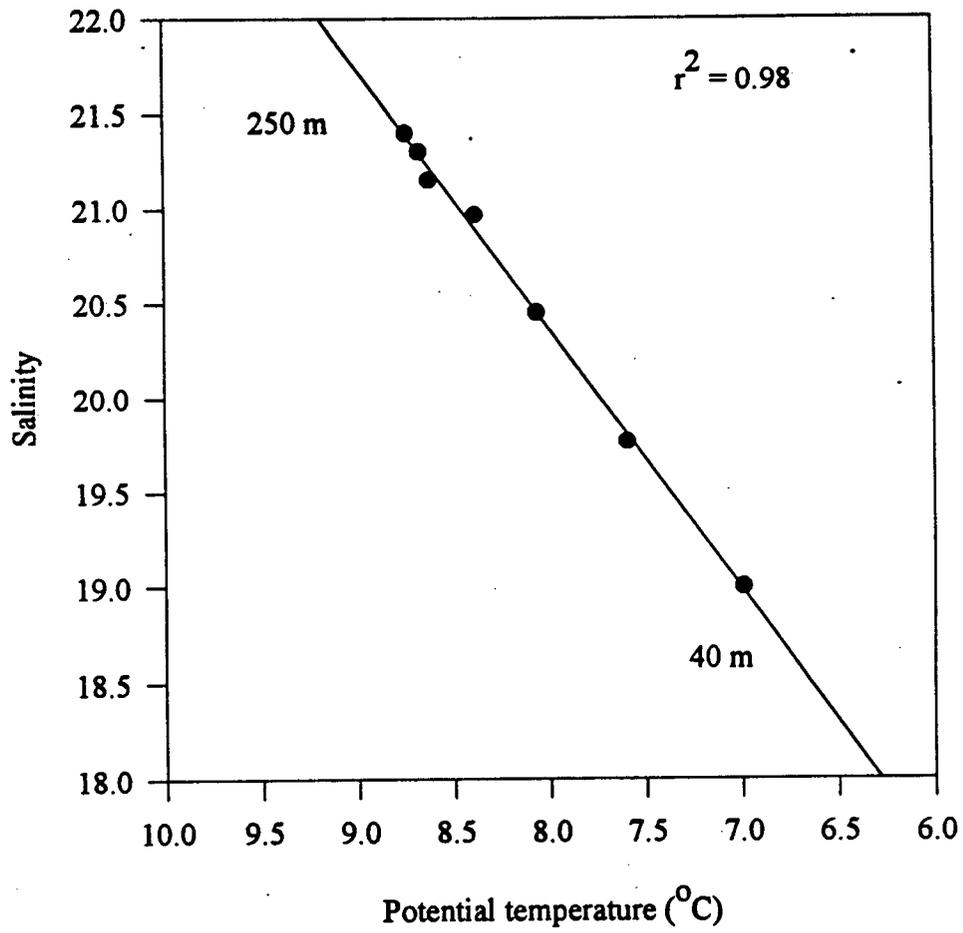


Figure 5.3.5.1 Potential temperature-salinity relationship for Station BS3-6

be constant with depth. A K_z value of $0.39 - 0.69 \text{ m}^2 \text{ d}^{-1}$ was calculated for the 40-250 m depth interval by Lewis and Landing (1991) assuming steady-state and insignificant contributions from horizontal mixing terms. Given the assumptions, the diffusion and reaction equation can be written as:

$$0 = K_z (\partial^2[C]/\partial z^2) - k_r C \quad \text{Equation 2}$$

Such an equation was used to model the oxidation of iodide as it diffused upwards from deep water (Tsunogai, 1971) and to estimate the oxidation rate of dissolved Mn in a meromictic lake (Balistrieri *et al.*, 1994). The solution to Equation 2 is given by (Tsunogai, 1971):

$$C = C_0 \exp - (k_r/K_z)^{1/2} z \quad \text{Equation 3}$$

where C_0 is the observed Cr concentration at the lower depth ($z = 0$), z is the distance above $z = 0$, K_z is the vertical eddy diffusion coefficient, k_r is the pseudo-first order reaction constant and it is assumed that horizontal gradients are zero. Using the observed Cr concentration for station BS3-6, and a K_z value of $0.52 \text{ m}^2 \text{ d}^{-1}$, the residence time, ($\tau = 1/k_r$) for chromium can be calculated for the suboxic zone (80-110 m) and for other depth zones in the vicinity of the redox interface (Table 5.3.5).

Depth range (m)	k_r (1/y)	τ (years)
45-80 (Oxic zone)	0.02343	42.7
80-110 (Suboxic zone)	0.02849	35.1
110-170 (Anoxic zone)	0.00093	1080

Table 5.3.5 Vertical diffusion reaction model results for Cr at station BS3-6 in the Black Sea.

As can be seen in Table 5.3.5, the estimated Cr residence time in the Black Sea is lowest in the suboxic zone and highest in the anoxic sulfidic waters. The Cr residence time above the interface is only slightly longer than in the suboxic zone. Thus the most intense Cr cycling occurs across the oxic-suboxic interface and results in removal as a result of reduction of Cr(VI) to Cr(III) with subsequent loss of Cr(III) via sorption. Dissolved Cr as Cr(III) is stable in the anoxic waters (presumably as organic and/or colloidal complexes) and consequently there is little removal in this region leading to the longer residence times observed.

5.3.6 Summary and Conclusions

Total dissolved chromium in the Black Sea shows higher values in the oxic region which decrease to a minimum at the interface and increase again into the suboxic and anoxic regions. The main factors controlling the distribution appear to be Cr redox reactions coupled with sorption onto particles at the interface. Cr(VI) is likely reduced to Cr(III) at the oxycline; this species is strongly particle reactive and is scavenged by organic matter in association with Mn and Fe oxyhydroxides. When the sinking particles undergo dissolution and/or reduction in the suboxic and anoxic regions, the sorbed Cr is released. By analogy with Saanich Inlet results, the reduced Cr(III) is likely present in the anoxic zone as colloidal and/or organic complexes. These complexes can undergo degradation to release inorganic Cr(III) during storage at low pH or by hydrogen peroxide oxidation and irradiation with UV light. The Cr residence time in the Black Sea interface region and in the oxic zone immediately above is calculated to be ~ 40 yrs and that in the anoxic region is estimated to be ~ 1000 yrs. Cr removal via redox and sorption processes in the vicinity of the interface is a much faster process compared to the anoxic region where reduced Cr(III) species appear quite stable.

Section II: Chromium distribution at the Juan de Fuca Ridge

5.4 INTRODUCTION

The penetration of sea water through the oceanic crust at ocean-ridge spreading centers can lead to high-temperature water-basalt interactions, producing hydrothermal fluids that are returned to the ocean through vents at the sea floor. The chemical processes that occur have been extensively described by, among others, Edmond *et al.* (1979, 1982), Von Damm *et al.* (1985 a, b) and Bowers *et al.* (1985). The hot, buoyant water emanating from vents rises tens to hundreds of meters above the sea bed before attaining density stability and spreading laterally, with large amounts of water from deeper in the water column being entrained in the process (Lupton *et al.*, 1985). These processes have been observed to produce large anomalies in the concentrations of various dissolved and particulate seawater constituents in areas of hydrothermal activity in both the Atlantic and Pacific oceans. For instance, hydrothermal vents are a major source of manganese to the oceans. Concentrations of manganese in the high-temperature hydrothermal fluids have been reported to range from 0.13 to 1.5 mmol/kg (Von Damm *et al.*, 1985 a, b; Klinkhammer and Hudson, 1986), six orders of magnitude higher than those in ocean-bottom waters. Thus submarine hydrothermal fluids at ocean ridges are an important source of elements to the oceans and can contribute significantly to the chemical mass balance of seawater. Hydrothermal activity can also be a major sink for some elements in seawater, e.g. magnesium.

Little is known about the effect of ridge crest hydrothermal activity on the distribution of dissolved Cr species in the resultant hydrothermal plumes. In a study of hydrothermal samples from the East Pacific Rise (EPR), Jeandel and Minster (1984) reported a maximum total dissolved Cr enrichment of six times the average seawater value in pure vent fluids. Values of the different dissolved Cr species were, however, not reported. In the present study, the concentration of Cr species at a station in the Juan de Fuca Ridge (JDFR) was investigated in order to assess the effect of hydrothermal activity on the distribution of this element.

5.5 Study Site

The Juan de Fuca Ridge system (Figure 5.5.1) is an active spreading center located approximately 500 km from the Washington and Oregon coasts between the Blanco and Sovanco fracture zones. It is a 600 km long, medium rate spreading center, with a spreading rate of 6 cm yr⁻¹. It is characterized by a narrow, approximately 1-2 km wide, well-defined, symmetrical axial valley with volcanic activity on the center of a broad ridge (Vogt and Johnson, 1973; Delaney *et al.*, 1981) rather than along a central graben. Numerous seamounts in a quasi-linear chain west of the ridge are described as being produced by a deep mantle "hot spot" that is interacting with other ridge formation processes (Morgan, 1972, 1973; Vogt and Johnson, 1973; Vogt and Byerly, 1976). Water column anomalies and extensive venting have been observed throughout the JDFR axis.

5.6 Sampling and Analytical Procedures

Samples were collected at station JDFR-1 (46°04.3 'N, 129°55.7'W; 2318 m depth) (Figure 5.5.1) over the Juan de Fuca Ridge in July 1992 by Rick Thompson and Brenda Burd from the Institute of Ocean Sciences (IOS), Sidney, B.C. Seawater samples were collected using 10 L acid-washed Teflon[®]-lined Go-Flo bottles suspended on a Kevlar line and triggered using Teflon[®] messengers. Subsamples for Cr were drawn using acid-cleaned Teflon[®] tubing and frozen immediately onboard with an acetone-dry ice bath. They were subsequently stored frozen in a ship-board freezer until analysis. In the shore-based laboratory, samples were allowed to thaw out on the bench for ~ 1 hr prior to analysis, after which Cr determinations were made using the electron capture detector gas chromatographic (ECD-GC) technique (Mugo and Orians, 1993).

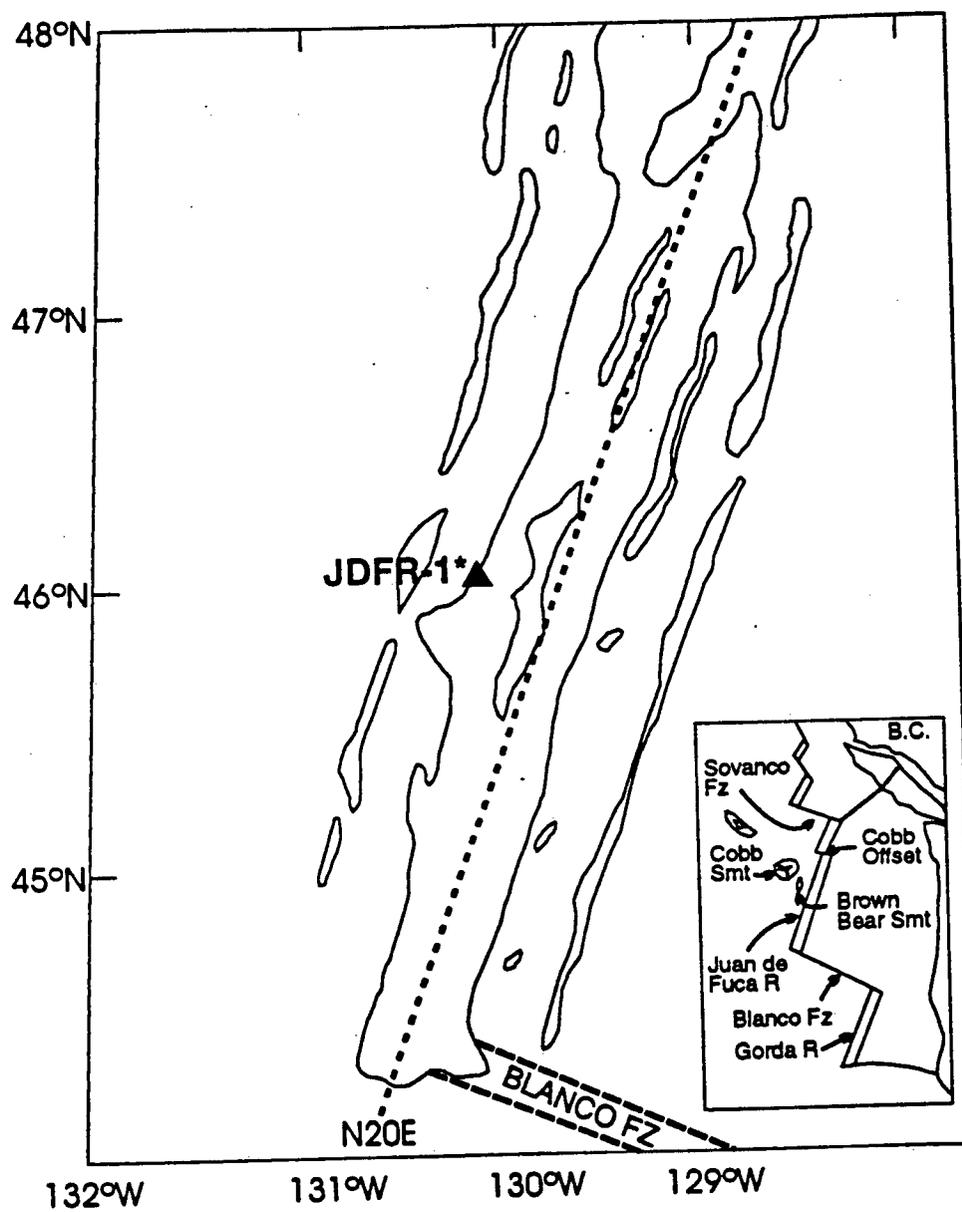


Figure 5.5.1 Sampling location (station JDFR-1) on the Juan de Fuca Ridge.

5.7 RESULTS and DISCUSSION

Chromium species distribution at station JDFR-1 are plotted as a function of depth in Figure 5.7.1a. Both Cr(VI) and total labile Cr show a slight surface depletion, as seen in typical open ocean regions, which could be from surface Cr biological uptake or from redox and scavenging processes. Total labile Cr ranged from 4.3 to 6.4 nM with Cr(VI) (3.0-5.5 nM) as the dominant dissolved Cr species. The main feature in the distribution is the increase in Cr(VI) and total labile Cr towards the bottom. Total labile Cr values increase from 4.0 nM at 1400 m to a high of 6.4 nM at 1810 m, with a deep water average (below 1600 m) of 6.0 nM.

To assess the effect of hydrothermal activity on the distribution of Cr at JDFR-1, the distribution of Cr species at station P in the eastern North Pacific, an area with no known hydrothermal activity, is shown in Figure 5.7.1c. A comparison of Cr profiles at the two stations shows that total labile Cr concentrations increase in bottom waters at both stations; however, the increase at the JDFR station is more pronounced and the observed maximum is above the bottom i.e., in a plume. Labile Cr(III) concentrations at the JDFR-1 are almost an order of magnitude higher than at Station P, with a range of 0.91 to 1.7 nM (20-28 % of total labile Cr), but close to the values measured in three B.C. inlets (Chapter 3). The observed high labile Cr(III) values may be of hydrothermal origin resulting from mixing of Cr-rich plume fluids with ambient seawater, a process which can be intensified due to coastal upwelling effects. Total dissolvable manganese levels at several stations in the JDFR are reported to be similarly enriched even at shallow depths, being 5-10 times greater than normal Pacific Ocean values (Jones *et al.*, 1981).

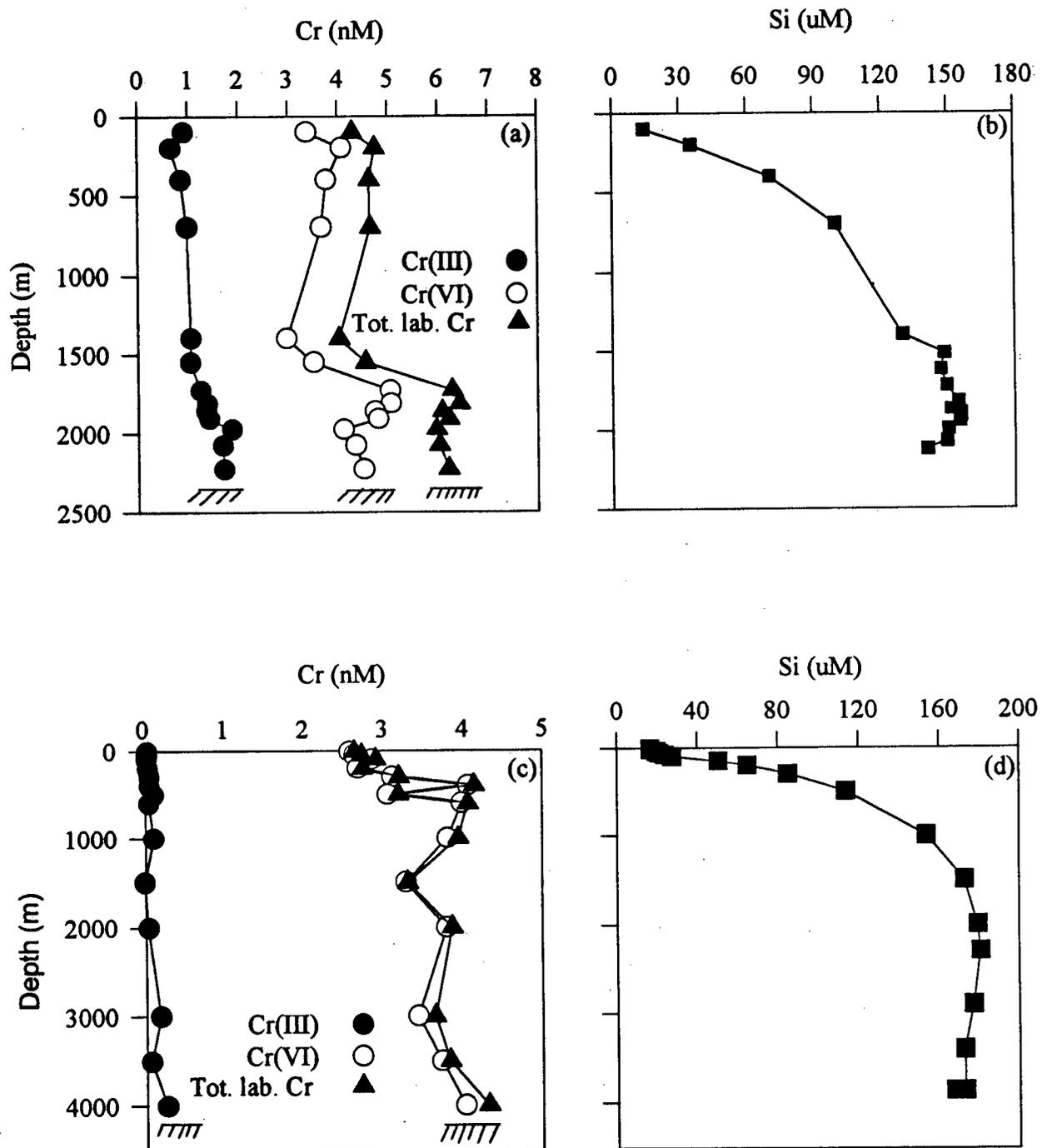


Figure 5.7.1: (a) Chromium species at Station JDFR-1 in the Juan de Fuca Ridge
 (b) Si data from JDFR-1 (c) Chromium species at Station P in the eastern North Pacific
 (d) Si data from Station P.

Thermodynamic considerations favor the dominance of Cr(III) in vent fluids (hot, acidic, sulfidic) from the JDFR. Ambient seawater, on the other hand, is cold, oxygenated and alkaline and under these conditions chromate is the dominant species. Assuming that plume fluids are enriched in Cr, their interaction with ambient seawater should potentially add Cr to seawater either as poorly soluble Cr(III) hydroxides or as soluble Cr(VI) after oxidation of vent-derived Cr(III). As particulate Cr analysis was not conducted on these samples, it is not possible to assess to what extent precipitation of Cr hydroxides occurs, and what effect this may have on the observed distribution of chromium species in the overlying water column at the JDFR. The fact that an increase in Cr concentration in deep waters at the JDFR is seen, however, suggests that hydrothermal activity may be a source of dissolved Cr.

Hydrothermal vent fluids at the JDFR axis contain, on average, ~ 1.10 mmol silica/kg seawater (Chase *et al.*, 1985). Assuming only two endmembers, and using silica data from station JDFR-1 (Figure 5.7.1b), an estimated composition of 3 % primary fluid and 97 % seawater is obtained for plume waters at 1550-1910 m depth. Thus an estimate of 78 ± 9 nM total labile Cr in pure JDFR vent fluids is obtained, much higher than the 16 nM reported for "pure" hydrothermal fluids at the EPR (Jeandel and Minster, 1987). Because of the tendency of Cr(III) species to bind to particles, Cr behavior during the mixing process is not expected to be conservative. As such, this value must be considered a minimum estimate of total labile Cr in these vent fluids.

Uptake of Cr and other trace metals by hydrothermal precipitates formed during the mixing process was suggested in the Mid-Atlantic Ridge (MAR) (Trochine and Trefry, 1988) and also in samples from the North Cleft Segment of the JDFR (Feely *et al.*, 1994). Particulate Cr data from the TAG hydrothermal field at 26°N in the MAR were 200 times greater near vent waters than MAR background values, suggesting that some of the particulate Cr enrichment was associated with hydrothermal activity. Dissolved Cr analyses were not conducted on the samples, so it is impossible to assess whether the particulate Cr signature was as a result of uptake from vent fluids or seawater, although the authors favored the latter explanation. If uptake were to occur from seawater rather than from vent fluids, one might expect lower dissolved Cr values

near vent areas. The fact that the observed total labile Cr concentrations from station JDFR-1 show enrichment relative to ambient seawater, however, argues against uptake from seawater as a likely explanation.

Remobilization of Cr can occur in metalliferous sediments near vent areas leading to higher bottom water values as suggested for the EPR (Jeandel and Minster, 1984). A likely Cr remobilization mechanism in the sediments is via oxidation of Cr(III) to Cr(VI) by Mn-oxides and subsequent diffusion of Cr(VI) into the water column. The Cr content of metalliferous sediments is 5-50 ppm (Bostrom and Peterson, 1969; Dymond *et al.*, 1973; Hoffert *et al.*, 1980). Thus the observed Cr enrichment of ~ 2.5 nM in the JDFR bottom waters relative to ambient seawater can conceivably be provided through release from metalliferous sediments. It is, however, difficult to use this source to explain the location of the observed maxima at JDFR-1 above the sea floor, i.e., in a plume. Thus these preliminary results suggest that hydrothermal activity may be a significant source of Cr at the JDFR.

5.8 Summary and Conclusions

Chromium values at a station in the Juan de Fuca Ridge showed enrichment (~ 1.5-2.0 times) over values from the open ocean in areas with no known hydrothermal activity, suggesting that vent fluids may be a source of Cr to these waters. The concentration of Cr in vent fluids is estimated to be 78 ± 9 nM, based on a composition estimate of 3 % primary fluid and 97 % seawater obtained using Si data. Since Cr behavior during the mixing and entrainment process is unlikely to be conservative, as a result of the particle reactive nature of Cr(III), this must be taken as a minimum estimate.

These preliminary results suggest that hydrothermal activity may be a source of Cr for bottom waters at the JDFR. More studies will be needed to decipher the extent and influence of hydrothermal activity on the Cr oceanic balance. In particular studies involving sampling of pure vent fluids, hydrothermal plumes, ambient seawater and the use of sediment traps near vent areas are needed to fully address this issue.

Chapter 6

Laboratory Studies of Chromium Transformations

6.1 INTRODUCTION

Thermodynamic calculations used to assess Cr speciation in seawater (Elderfield, 1970) show that at equilibrium, dissolved Cr should be present almost entirely as Cr(VI). Field observations, however, show that even though Cr(VI) is the dominant oxidation state, Cr(III) is always present in measurable concentrations particularly in nearshore and surface waters (Chapters 3, 4). This contradiction between field results and equilibrium speciation predictions suggests that thermodynamic considerations alone are inadequate. The kinetics of the main reactions which control the chromium cycle in natural waters therefore warrant investigation. Two aspects of Cr aquatic chemistry that require further study are the kinetics of Cr redox reactions and the role of dissolved organic matter (DOM) in Cr speciation either as a reductant and/or complexing agent for Cr(III) species in solution.

Cr(III) oxidation reactions are reported to be quite slow. Schroeder and Lee (1975) obtained a pseudo-first-order rate constant of 0.37/yr for the oxidation reaction with O₂, but Eary and Rai (1987) did not observe any oxidation with O₂ at 27 °C after 24 hours. The oxidation of Cr(III) by manganese oxides is reported to be more rapid than by dissolved oxygen, but the reaction rates depend on the solution chemistry and on the Mn oxides used. Second-order rate constants with respect to Mn oxide and Cr(III) ranging from 0.0008 M⁻¹ s⁻¹ for γ -MnOOH (Nakayama *et al.*, 1981b) to 1.34 M⁻¹ s⁻¹ for an unspecified oxide (Schroeder and Lee, 1975) have been observed.

Many chemicals may reduce Cr(VI) to Cr(III) in water or inside the cells of organisms. These include iron(II), sulfides, and some organic compounds such as fulvic acid, amino acids and carboxylic acids (Schroeder and Lee, 1975; Nakayama *et al.*, 1981a; Connett and Wetterhahn, 1985; Eckert *et al.*, 1990). Schroeder and Lee (1975) reported some results on the reduction of Cr(VI) with Fe(II) and H₂S in water samples but did not study the kinetics of the reduction as a

function of physical and chemical variables. Reduction of Cr(VI) by various organic compounds was shown by Nakayama *et al.*, (1981a) but no rate measurements were reported. Kinetic investigations by Pettine and Millerò (1994) revealed that the reduction of Cr(VI) by hydrogen sulfide was 2-3 times faster in seawater than in NaCl solutions.

The principal goal of this study was to investigate the interaction of humic acid with Cr species as 1) a reducing agent for Cr(VI) and 2) complexing agent for Cr(III). A preliminary study of Cr(VI) reduction by Fe(II) was also undertaken in addition to a mixing experiment involving field samples from Saanich inlet. The results of these laboratory studies are used to evaluate the role of these interactions in Cr speciation and to assess their influence on the geochemistry of this element in seawater.

6.2 I: Kinetic Investigation of Cr(VI) Reduction by Humic Acid

6.2.1 Humic Acids

"Humic substances" are complex, largely uncharacterised, organic polymers which comprise a sizable fraction of the organic matter in the oceans. They have a wide range of molecular weights extending from a few hundreds to several hundred thousands. The mechanism of their formation is unknown, although suggestions have been made (Gjessing, 1976; Harvey *et al.*, 1983; Bjornsen, 1988), and the material can have either a terrestrial or a marine source. Although they have very different structures, the terrestrial and marine humics are thought to contain similar functional groups (double bonds, quinone groups, phenolics, hydroxyls, carbonyls, etc.) and thus display similarities in their reactivities (Zepp *et al.*, 1981). In addition, a large amount of terrestrial humic acids are present in coastal marine environments.

The acidic character of humic acids is attributed mainly to the presence of O-containing functionalities, primarily carboxyl and phenolic hydroxyl groups, and the occurrence of quinones and polyhydroxy phenols is thought to be, at least in part, responsible for their reducing abilities. Traditionally, humic substances are extracted from soils, peats or sediments by fairly strong alkaline solutions. This extraction procedure leads to an empirical fractionation scheme based on their pH-dependent solubility behavior (Figure 6.2.1.1).

Humic acids are the portion which is extractable (generally by alkaline aqueous solutions) and precipitated at low pH, while fulvic acids remain in solution under the same conditions. Humic acids can participate in the cycles of trace elements as reductants, e.g. Fe^{3+} to Fe^{2+} (Szilagyi, 1971) or as complexing agents (e.g. Saxby, 1969). Another important property of humic substances is their role in oceanic photochemical reactions. Photochemically induced reduction of Mn oxides by humic substances is, for instance, thought to be responsible for the dissolved manganese maximum in surface waters (Sunda *et al.*, 1983). Indirect photoreduction of Cr(VI) with the involvement of Fe(II) and dissolved organic matter has also been suggested as a possible control on Cr speciation and concentrations in surface waters (Kieber and Helz, 1992).

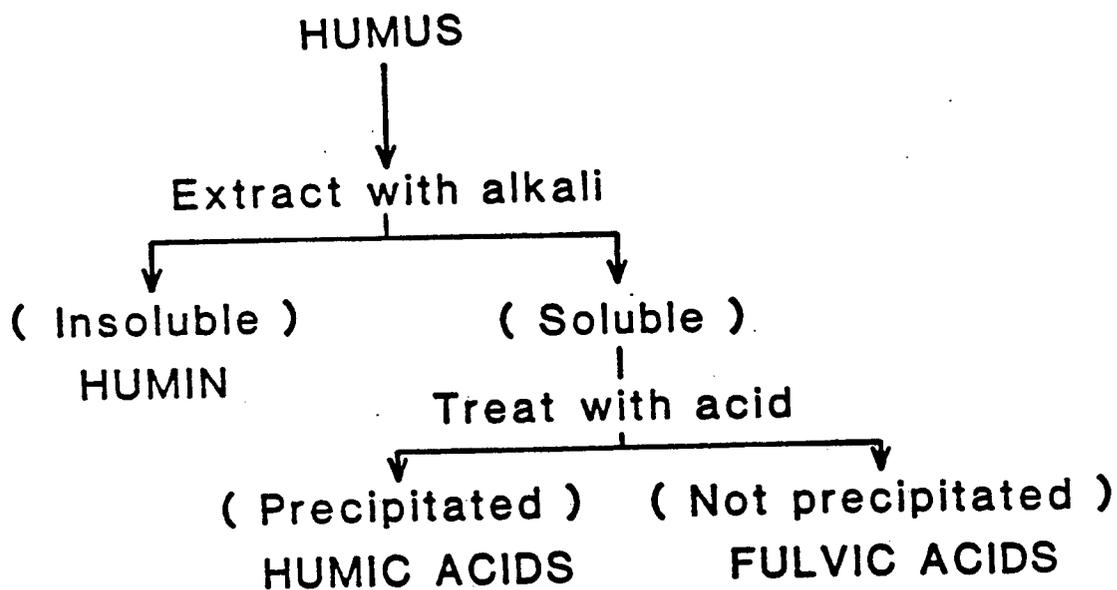


Figure 6.2.1.1 Fractionation of humic substances on the basis of their pH-dependent solubility properties (from Francoise, 1987).

6.3 MATERIALS and METHODS

Kinetic studies of Cr(VI) reduction by humic acid (HA) were conducted using seawater samples spiked with a stock Cr(VI) standard (20 ppb). Oxidic seawater was collected from a depth of 50 m in Saanich Inlet in July 1994, using trace metal clean techniques as described in Chapter 4 and stored frozen. The humic acid used in this study was obtained from the Aldrich Chemical Company (Milwaukee, Wisconsin) as a sodium salt. Stock HA solution (500 ppm) was prepared by dissolving 0.250 g of material in 2 mL of a 0.1 M NaOH aqueous solution and shaking thoroughly on the shaker for a few minutes (Selli *et al.*, 1996). It was then diluted to 500 mL with DDW, the pH adjusted to ~ 7.0 and subsequently stored in the fridge with further dilutions before use as necessary.

The reaction vessel consisted of an acid-washed 1 L Teflon[®] bottle equipped with a Teflon[®]-coated magnetic stirrer. The stock 20 ppb Cr(VI) standard was spiked into ~ 1 L seawater to give a final total labile Cr concentration of approximately 20 nM. The spiked seawater was then stirred for ~ 3 hrs to allow equilibration of spike and seawater. Reductions were initiated by adding a known amount of humic acid to the reaction vessel, with continuous stirring maintained throughout. Control experiments were conducted in a similar manner but with no added humic acid. The progress of the reaction was monitored by withdrawing 15 mL subsamples from the reaction flask at different times using a long Eppendorf pipette and analyzing them for labile Cr(III) and total labile Cr using the electron capture detector gas chromatographic (ECD-GC) technique (Mugo and Orians, 1993).

To test the effect of light on the reduction, initial experiments were performed under both natural light as well as in light shielded (Al foil) conditions. Exposure to light had no noticeable effect on the reaction suggesting that photochemical reduction of Cr(VI) in the near-opaque Teflon[®] reaction vessel was negligible. In subsequent experiments, the vessel was therefore not shielded from light.

6.4 RESULTS AND DISCUSSION

6.4.1 Kinetic Analysis

Rates of reduction of Cr(VI) to labile Cr(III) with HA were carried out under conditions of excess HA (20-500 fold). Under these conditions, reaction kinetics were fixed with respect to the concentration of humic acid. The pseudo-first-order rate constant (k_{exp} , hr^{-1}) at an excess HA concentration is given by:

$$-d[\text{Cr(VI)}]/dt = k_1 [\text{Cr(VI)}] \quad \text{Equation 1}$$

and may be determined from a plot of $\ln [\text{Cr(VI)}]$ vs time. In the ECD-GC analytical scheme, labile Cr(III) and total labile Cr are measured directly as Cr-tfa complexes, with Cr(VI) obtained by difference. Because of the time required for replicate determinations during a kinetic run, in most experiments only the formation of labile Cr(III) fraction was investigated as a function of time. Preliminary runs at pH 4.2 showed an increase in labile Cr(III) that paralleled the decrease in Cr(VI) (Figure 6.4.1.1). After 4 hrs, > 95 % of the original Cr(VI) has been reduced to labile Cr(III). The total labile Cr in the reaction vessel remains approximately constant suggesting that other than Cr redox transformations, no significant loss ($\pm 2\%$) of either species occurs during the time scale of the reaction. The rate of reduction of Cr(VI) decreases with time. The linearity of logarithmic first order plots for 0-4 hrs verify the suitability of the pseudo-first order assumption for this time interval (Figure 6.4.1.2). It was only when the reaction mixture was left to stand on the bench for several days that a decrease in labile Cr(III) over time was observed suggesting possible complexation of Cr species with humic acid (this was investigated in a separate experiment - see below).

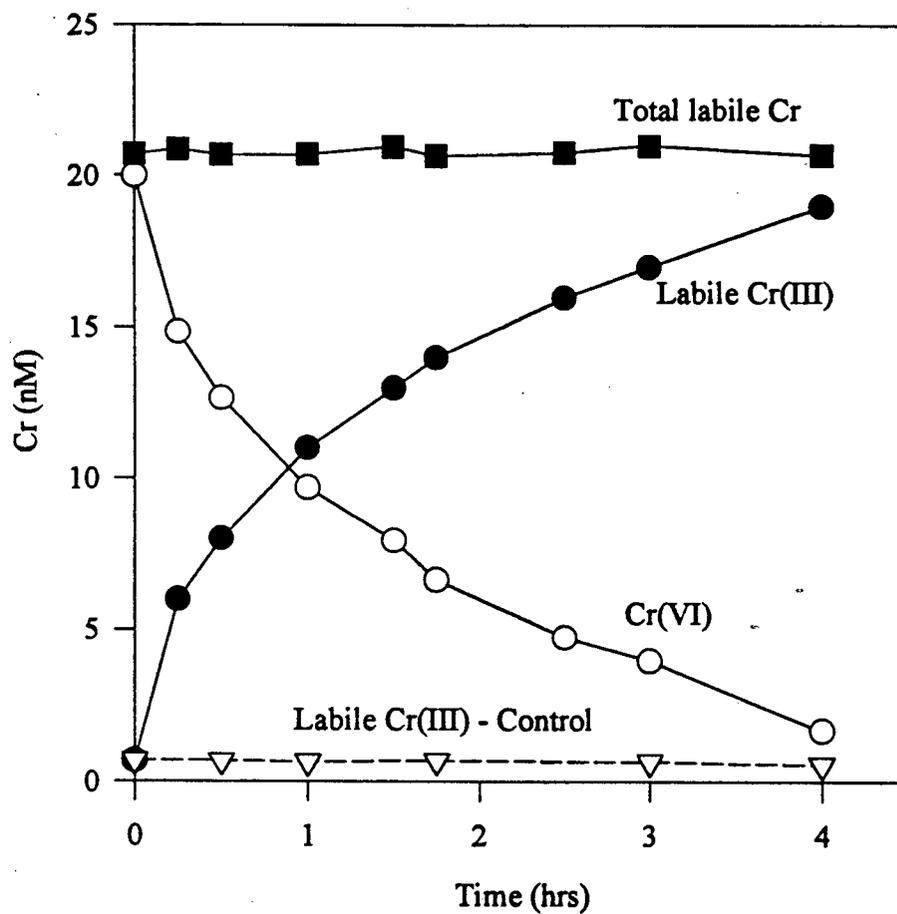


Figure 6.4.1.1 Chromium species as a function of time in a typical experimental system at pH 4.2, $[\text{Total Cr}]_0 = 20 \text{ nM}$, and $[\text{HA}] = 400 \text{ nM}$. Cr(III) and totalCr are determined directly by the ECD-GC technique with Cr(VI) obtained by difference (see text).

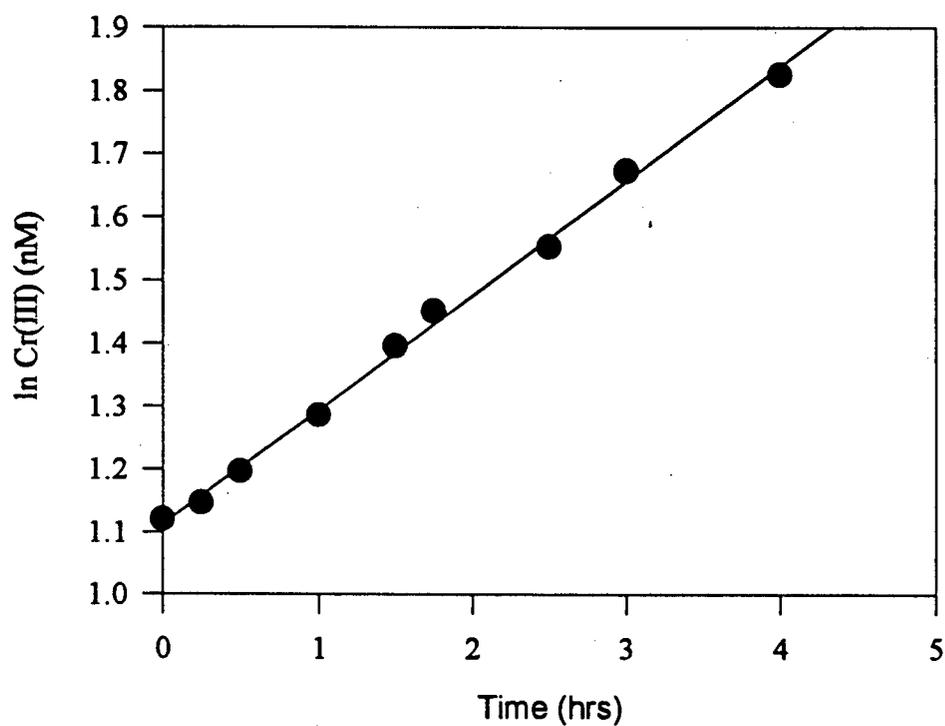


Figure 6.4.1.2 Pseudo-first order rate plot of $\ln[\text{Cr(III)}]$ versus time for Cr(VI) reduction by excess [HA] at 25 °C and pH 5.2

The slope of the line equals the pseudo-first order constant

k_{exp} (defined in text), $r^2 = 0.99$, $[\text{HA}] = 400 \text{ nM}$, $[\text{Total Cr}]_0 = 20 \text{ nM}$

A typical run at 25 °C, pH = 4.2, [Cr(VI)] = 20 nM and [HA] = 400 nM yielded $k_1 = 0.36 \pm 0.007 \text{ hr}^{-1}$ ($t_{1/2} = \ln 2 / k_{\text{exp}} = 116 \pm 2.26 \text{ min}$). Several sets of experiments were conducted to determine the effects on the reduction of Cr(VI) due to various solution parameters. The parameters investigated included the concentrations of humic acid, pH and temperature.

6.4.2 Effect of pH

The effect of pH on k_1 was examined over a wide pH range of 2.5 to 8.2 (ambient seawater pH) at 25 °C, [Cr(VI)] = ~ 20 nM and [HA] = 20 μM . The pH was changed by adding varying amounts of dilute HCl, CH₃COOH and a NaAc/HAc buffer system. Similar to the results of Cr(VI) reduction with fulvic acid (Eckert *et al.*, 1990) no Cr(VI) reduction was observed above neutral pH; the reaction rate, however, increased with decreasing pH below 6.5. Thus chromate reduction by humic acid is dependent on the hydrogen ion activity (Figure 6.4.2.1). Linear regression of the logarithm of the rates determined between pH 2.5 and 6.5 gives a reaction order with respect to [H⁺] of 0.23 ± 0.01 (Figure 6.4.2.2). Subsequent kinetic runs were conducted at pH 4.2.

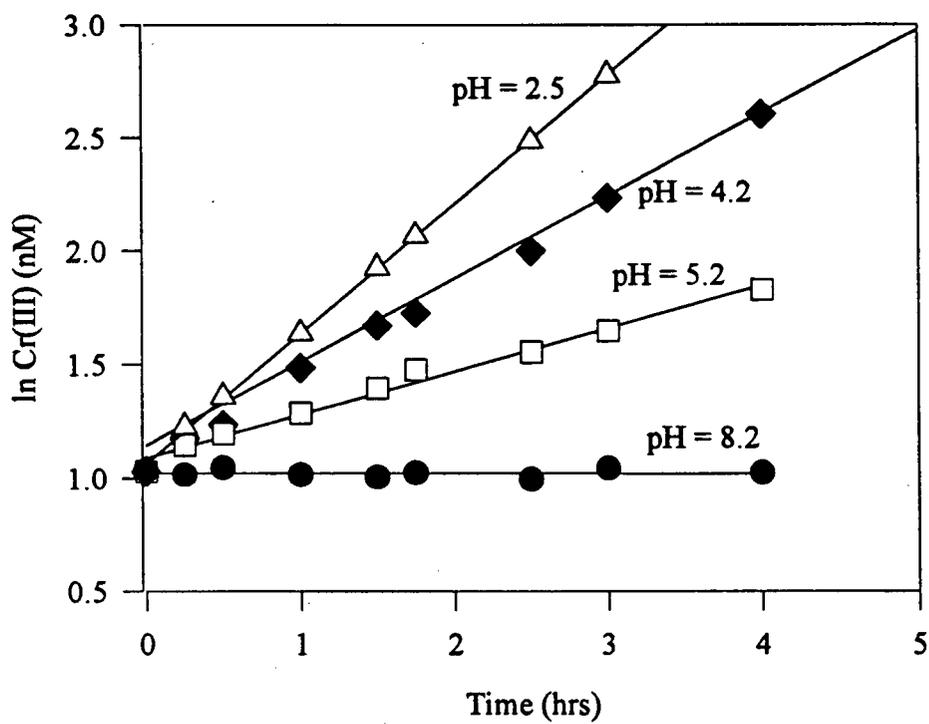


Figure 6.4.2.1 Values of $\ln [\text{Cr(III)}]$ versus time for the reduction of Cr(VI) with $[\text{HA}]$ at different pH values, $[\text{Total Cr}]_0 = 20 \text{ nM}$, $[\text{HA}] = 400 \text{ nM}$, 25°C .

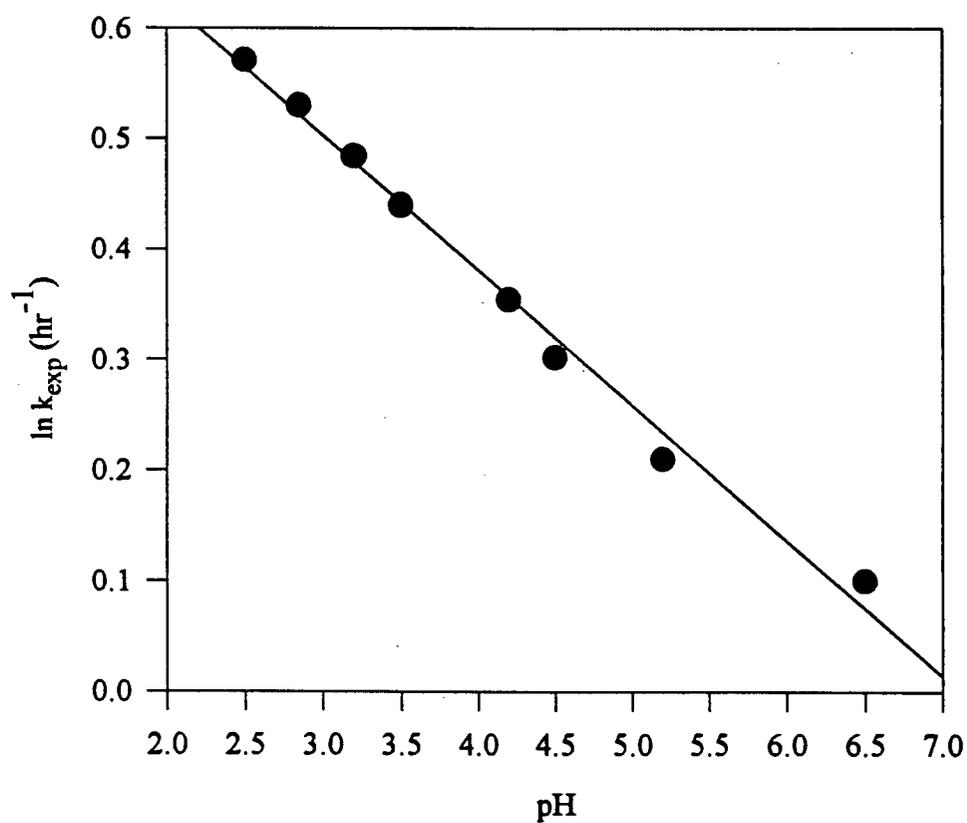


Figure 6.4.2.2 Values of $\ln k_{\text{exp}}$ for the reduction of Cr(VI) (21 nM) with HA (400 nM) at 25 °C as a function of pH. The reaction order with respect to the hydrogen ion activity equals the slope of the plot.

The transformation of Cr(VI) as CrO_4^{2-} or HCrO_4^- to Cr(III), which is produced as the octahedral complex, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, converts an oxyanion to a hydrated cation. The net reaction therefore consumes hydrogen ions and it is therefore expected that the reaction rates should increase with higher hydrogen ion concentrations as observed here. The transfer of a proton to the hydroxy ligand on the hydrogen chromate was proposed as the rate-determining step in substitution reactions of hydrogen chromate with acidic ligands (Connett and Wetterhahn, 1985, 1986). It was also suggested that the reduction of chromate by thiols involves the attack of CrO_4^{2-} by the unionized thiol which transfers a proton to an oxygen atom of the chromate as part of the rate-limiting step; the subsequent protonation of OH^- facilitates its loss (Connett and Wetterhahn, 1985). Similar mechanisms may apply here for the reduction of Cr(VI) by HA, given the difficulties of representing the general acid-base chemistry of humic acid and particularly the specific moieties involved in Cr(VI) reduction.

A non-integer value for the reaction order with respect to $[\text{H}^+]$ was also reported for the reduction of Cr(VI) with substituted phenols (Elovitz and Fish, 1994) and for Cr(VI) reduction by soil fulvic acids (SHAs) (Wittbrodt and Palmer, 1996). Elovitz and Fish (1994) found that the rate dependence of Cr(VI) reduction by phenols was governed by three parallel redox pathways involving zero, one and two protons with oxidation products suggesting the occurrence of both one- and two-electron transfer processes.

6.4.3 Effect of Temperature

The temperature dependence of Cr(VI) reduction by humic acid was studied in the 25-60 °C range using $[\text{Cr(VI)}] = 20 \text{ nM}$, pH 4.2 and $[\text{HA}] = 400 \text{ nM}$ (Figure 6.4.3.1). Pseudo first-order rate constants, k_1 , for the various temperatures were determined. The activation enthalpy and entropy for the reduction (ΔH^\ddagger , ΔS^\ddagger) were calculated using (Lasaga, 1981):

$$k_{\text{exp}} = k_b T / h [e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}] \quad \text{Equation 2}$$

where the enthalpy (ΔH^\ddagger) and entropies (ΔS^\ddagger) of activation were calculated from the slopes and intercepts of plots of $\ln(k_{\text{exp}}/T)$ versus $1/T$ (Figure 6.4.3.2). T is the temperature in kelvin, k_b is Boltzman's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), h is Planck's constant ($6.63 \times 10^{-34} \text{ J s}^{-1}$), and R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). Because of the empirical manner in which the rate coefficients are derived, the activation parameters must be taken as composite values for all reactions up to and including the rate-limiting step. As such they do not necessarily describe the activation energy of an elementary reaction step (McAuley and Olatunji, 1977). The computed enthalpy of activation ($67 \pm 4 \text{ kJ/mol}$) is similar to that obtained by Wittbrodt and Palmer (1996) for the reduction of Cr(VI) by soil humic acid ($61 \pm 3 \text{ kJ/mol}$).

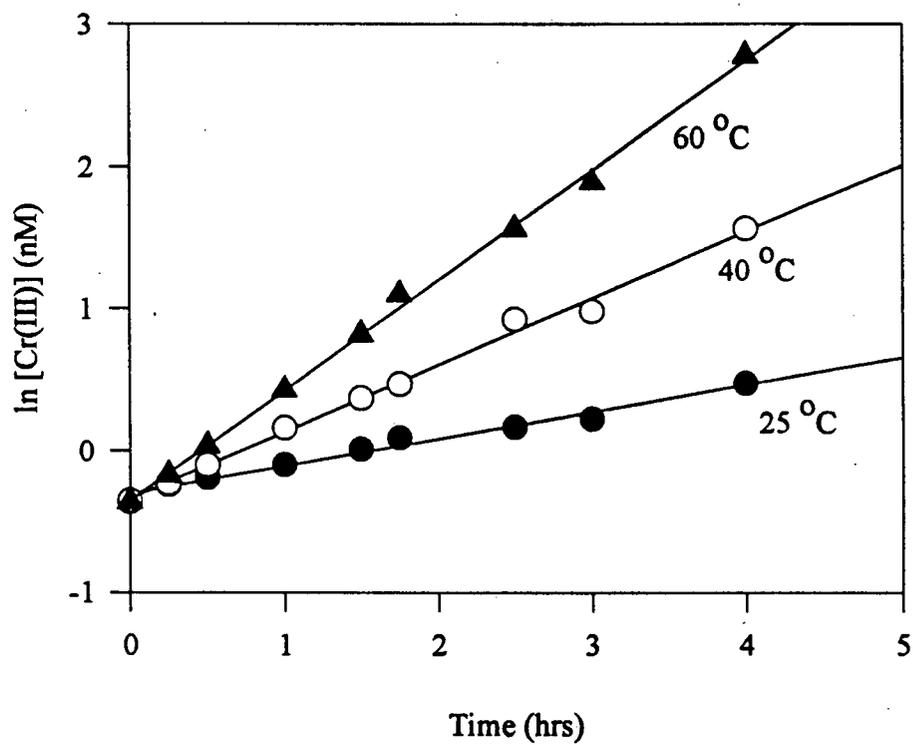


Figure 6.4.3.1 Pseudo-first order rate plots of $\ln[\text{Cr(III)}]$ versus time for Cr(VI) reduction by excess HA at 25, 40 and 60 °C.

$[\text{Total Cr}]_0 = 20 \text{ nM}$, $[\text{HA}] = 400 \text{ nM}$, $\text{pH} = 4.2$.

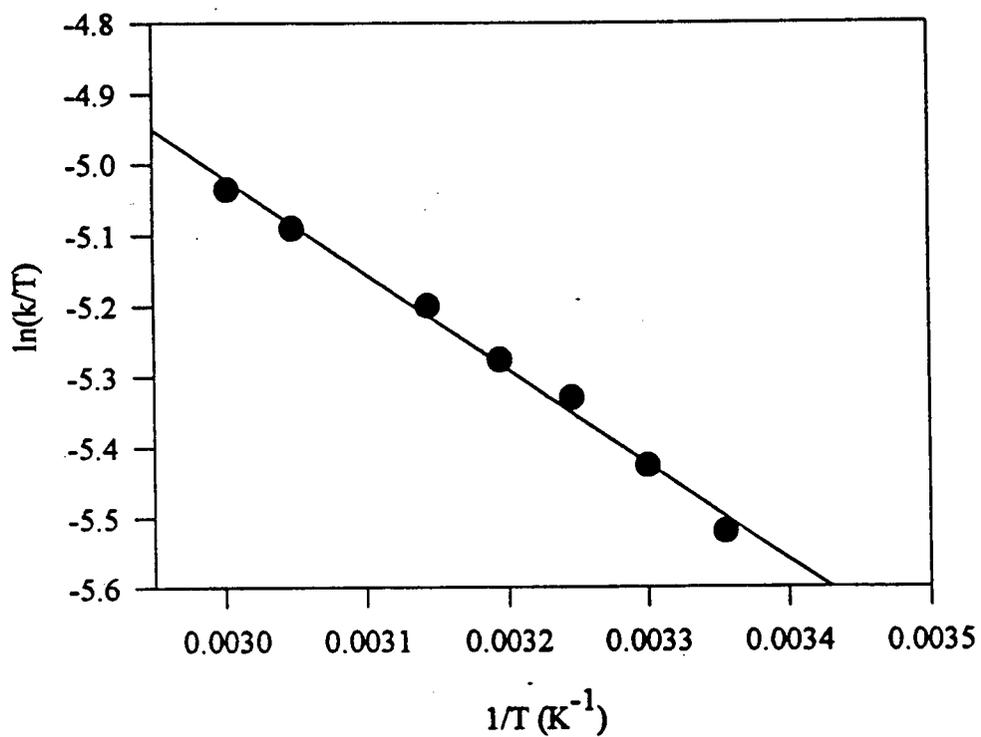


Figure 6.4.3.2 Influence of reaction temperature on the observed rate coefficients for Cr(VI) reduction by HA. Heat (H) and entropy (S) of activation are computed from the slope and intercept of the $\ln(k/T)$ vs. $(1/T)$ plot, respectively.

The calculated entropy of activation, ΔS^\ddagger , for the reduction of Cr(VI) by humic acid is $-158 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$ and is similar to those calculated for the reduction of Cr(VI) by 4-methylphenol (Elovitz and Fish, 1994) (-181 to $-185 \text{ J K}^{-1} \text{ mol}^{-1}$), benzyl alcohol (Gupta *et al.*, 1986) ($-180.8 \text{ J K}^{-1} \text{ mol}^{-1}$), and glutathione ($-167 \text{ J K}^{-1} \text{ mol}^{-1}$ - McAuley and Olatunji, 1977). ΔS^\ddagger is often used as an indicator of the configuration of the activated complex. A large negative number, such as that calculated for humic acid indicates that the reaction molecules are separated by short bonds, thus the decrease in entropy is large and the pre-exponential factor $[(k_b T/h) \exp(\Delta S^\ddagger / R)]$ is small. The energy of activation, E_a ($\Delta H^\ddagger - T\Delta S^\ddagger$) for the reduction of Cr(VI) by humic acid at 298 K is $112 \pm 4 \text{ kJ/mol}$, and is comparable to the $122 \pm 3 \text{ kJ/mol}$ value for the reduction of Cr(VI) by soil humic acid (Wittbrodt and Palmer, 1996).

6.4.4 Influence of the Reducing Agent

To investigate the effect of varying the concentration of the humic acid reducing agent, experiments were performed at 25 °C and at pH 4.2 over a large [HA] concentration range (400-2000 nM), a factor of 20-100 times greater than [Cr(VI)]. The slope of the best fit relating $\log k_1$ and $\log [\text{HA}]$ is equal to 0.96 ± 0.03 thus indicating a first order dependence of the reduction rate on [HA] (Figure 6.4.4.1).

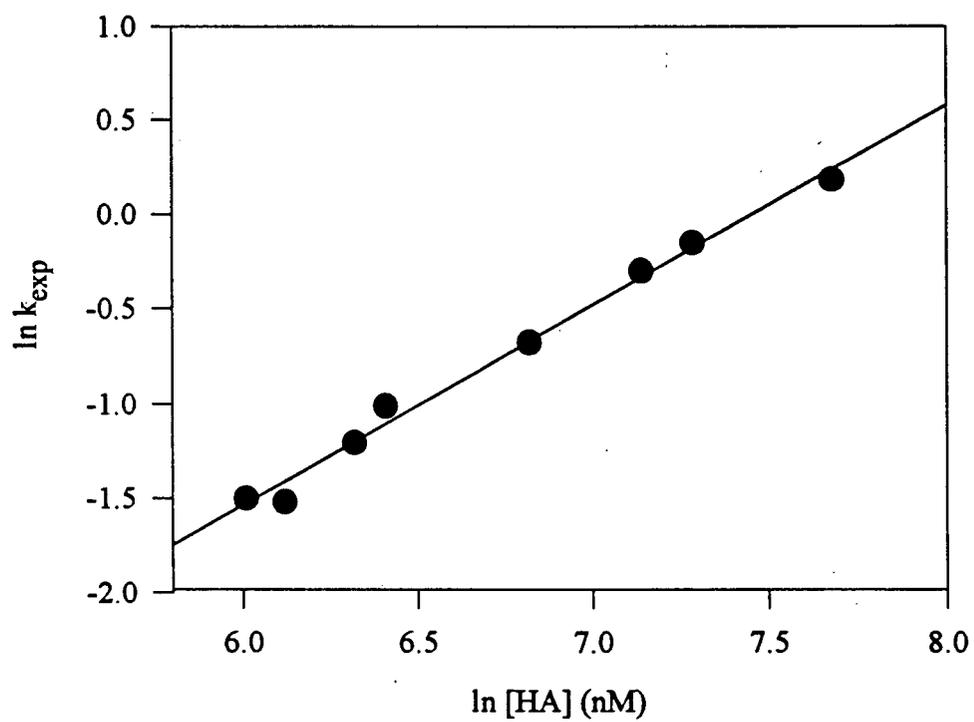


Figure 6.4.4.1 Values of $\ln k_{\text{exp}}$ as a function of $\ln [\text{HA}]$ at 25 °C and pH 4.2.

6.4.5 Characteristics of the Reaction

In developing a general rate law for the reduction of Cr(VI) by humic acid, reduction of Cr(VI) by simple organic compounds can be used as models. Studies of the reduction of Cr(VI) by alcohols (Lee and Stewart, 1967; Wiberg and Schafer, 1969; Sengupta *et al.*, 1986; Lee and Chen, 1991) and aldehydes (Graham and Westheimer, 1958; Gupta *et al.*, 1990; Alvarez-Macho *et al.*, 1990) indicate that the first step in the reduction is the formation of a chromate ester that is stabilized by intramolecular H-bonding.



The equations are written in terms of $[\text{HCrO}_4^-]$ because this is believed to be the reactive species in many Cr(VI) organic reactions and is also the predicted species at $\text{pH} < 6.5$ (Wittbrodt and Palmer, 1995). Chromate ester formation is believed to be fast and reversible. Elovitz and Fish (1994) found essentially instantaneous chromate-phenol ester formation in the pH range 2-5. The electron transfer occurs during the irreversible decomposition of the ester. The decomposition



is believed to be the rate-limiting step. The chromate ester formation is thought to be less dependent on pH than is the redox step (Elovitz and Fish, 1994). At constant pH, the rate of reduction of Cr(VI), R , should follow:

$$R = -k_d[\text{HCrO}_4^- \cdot \text{HA}] = -k_e K_e [\text{HCrO}_4^-] [\text{HA}] \quad \text{Equation 5}$$

where K_e is the equilibrium constant for the chromate ester formation ($= k_f/k_r$). Setting $(k_d K_e)$ equal to k_1 yields:

$$R = -d[\text{Cr(VI)}]/dt = -k_1[\text{HCrO}_4^-][\text{HA}] \quad \text{Equation 6}$$

Many Cr(VI)-organic reactions at constant pH have been reported to follow a rate equation similar to equation 6 with a first order dependence on both Cr(VI) and the organic compound (Wieberg, 1965). The empirical rate law for the reduction of Cr(VI) by humic acid may thus be written as:

$$R = d[\text{Cr(III)}]/dt = -d[\text{Cr(VI)}]/dt = -k_1[\text{HCrO}_4^-][\text{HA}] \quad \text{Equation 7}$$

Thus the rate equation reflects experimental observations of a first order dependence on both [Cr] and [HA], the empirical second order rate constant k_1 , is a function of pH. Due to the poorly defined structure of humic acid, this rate expression must ultimately be empirical rather than mechanistic. At a constant pH, this equation and a suitable value of k_1 will accurately predict the rate of Cr(VI) reduction. In a well buffered system in which pH varies little, and in the presence of excess [HA], the equation reduces to a first order expression in which the rate of chromate reduction is dependent on the initial concentration. This equation suggests therefore that in aquatic environments with high dissolved organic matter (DOM) concentrations and pH values below neutral (e.g. poorly buffered lake systems) one can expect to find considerably higher levels of labile Cr(III).

6.5 II: Chromium(III) Interactions with Humic Acid

Cr(VI) reacts rapidly with humic acid at moderately acidic pH, causing reduction of Cr(VI) to Cr(III), and presumably conversion of some of the HA components to oxidized products (Part I). In a typical run (pH = 4.2) over 95 % of the spiked Cr(VI) was reduced in about 4 hrs. Since the concentration of humic acid was greatly in excess of Cr, the excess HA was available at the end of the kinetic run to interact with the reduced labile Cr(III), presumably through complexation, in accordance with the known properties of Cr(III) (Osaki *et al.*, 1983; Douglas *et al.*, 1986). This was tested by periodically analyzing the reaction mixture for labile Cr(III) over the course of a week. The results for total labile Cr ~ 20 nM (pH = 4.2, 25 °C) show that the detected labile Cr(III) decreased with time over the course of several days. Since the ECD-GC technique measures "free" or labile Cr, these results suggest that labile Cr(III) available in the flask for complexation by the Htfa ligand decreases with time, presumably via binding by HA. An alternative pathway for the loss of labile Cr(III) is via sorption to particles and vessel walls.

To further investigate the observed labile Cr(III) loss, a second experiment was performed in which a Cr(III) standard (~ 20 nM) was spiked into seawater which had been stored acidified at pH ~ 2.5 for several months. After equilibration of spike and seawater, while stirring for 3 hrs, 400 nM HA was added to the reaction vessel and stirring continued. Subsamples were drawn from the flask at discrete time intervals and analyzed for labile Cr(III). A few subsamples were also analyzed for total oxidizable Cr after sample treatment with H₂O₂ and irradiation with UV light. In the control experiment, the Cr(III) spike was added but no HA additions were made. The results for measured Cr species are plotted in Figure 6.5.1.

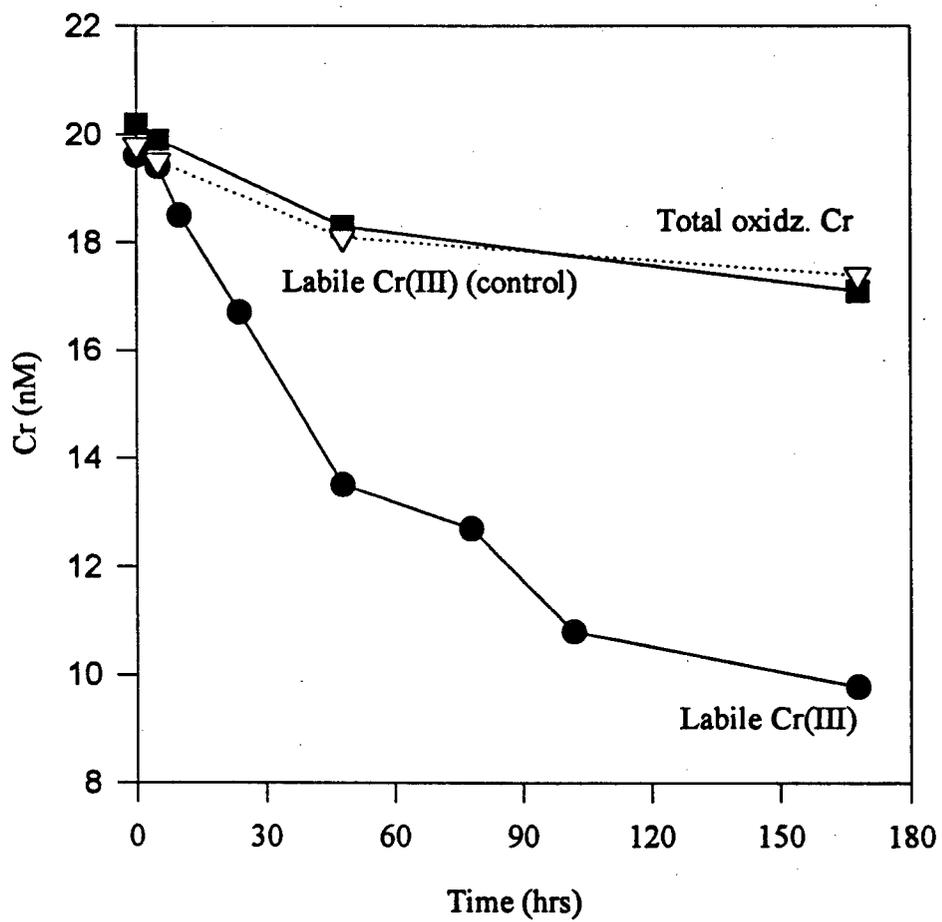


Figure 6.5.1 Influence of HA on Cr(III) spiked-seawater sample as a function of time. $[\text{Cr(III)}] = 20 \text{ nM}$, $[\text{HA}] = 400 \text{ nM}$, $\text{pH} = 4.5$, 25°C .

As can be seen from the plots, the labile Cr(III) detected by the ECD-GC in the presence of humic acid decreased by more than 50 % over a period of a week, whereas the total oxidizable Cr decreased by only 15 % over the same period. A similar experiment conducted with EDTA instead of humic acid resulted in a decrease of detected labile Cr(III) by as much as 10 % after 4 hrs (results not shown). These results confirm that humic acid is capable of binding Cr(III) as stable, organic chromium complexes in solution which cannot be detected by the ECD-GC procedure without further sample oxidation with H_2O_2 and irradiation with UV light. The observed 15 % loss of total labile Cr over the same period most likely results from Cr sorption to vessel walls or suspended particles in solution.

6.6 III: Chromium(VI) Reduction by Fe(II)

A preliminary investigation of chromate reduction by Fe(II) was conducted using a 1 L Teflon[®] reaction vessel similar to the one used for investigating the kinetics of Cr(VI) reduction by humic acid. Cr(VI) spikes (~ 21 nM) were allowed to equilibrate with seawater for two hours (at 25 °C with constant stirring) after which 400 nM of Fe(II) was added to the vessel. One experiment was conducted at pH 7.8, close to the pH of the seawater sample while the second experiment was conducted at pH 3.5. In the control experiments, Cr(III) was spiked into the seawater but no Fe(II) was added. Subsamples (15 mL) were withdrawn from the reaction vessel and analyzed for labile Cr(III) and total labile Cr by ECD-GC.

Cr(VI) reduction by the added Fe(II) was observed at both pH values relative to the control (Figure 6.6.1). At pH 7.8 ~ 23 % the Cr(VI) was reduced within 20 minutes whereas reduction was complete at pH 3.5 within the same period. No changes were observed in the control experiments. Thus Cr(VI) reduction by Fe(II) is favored at low pH, and it also appears to be much faster than reduction by humic acid at approximately the same conditions. These results are in agreement with the findings of various workers which show that Fe(II) is an efficient reductant for Cr(VI) under a variety of conditions (e.g. Schroeder and Lee, 1975; Saleh *et al.*, 1989, Eary and Rai 1989).

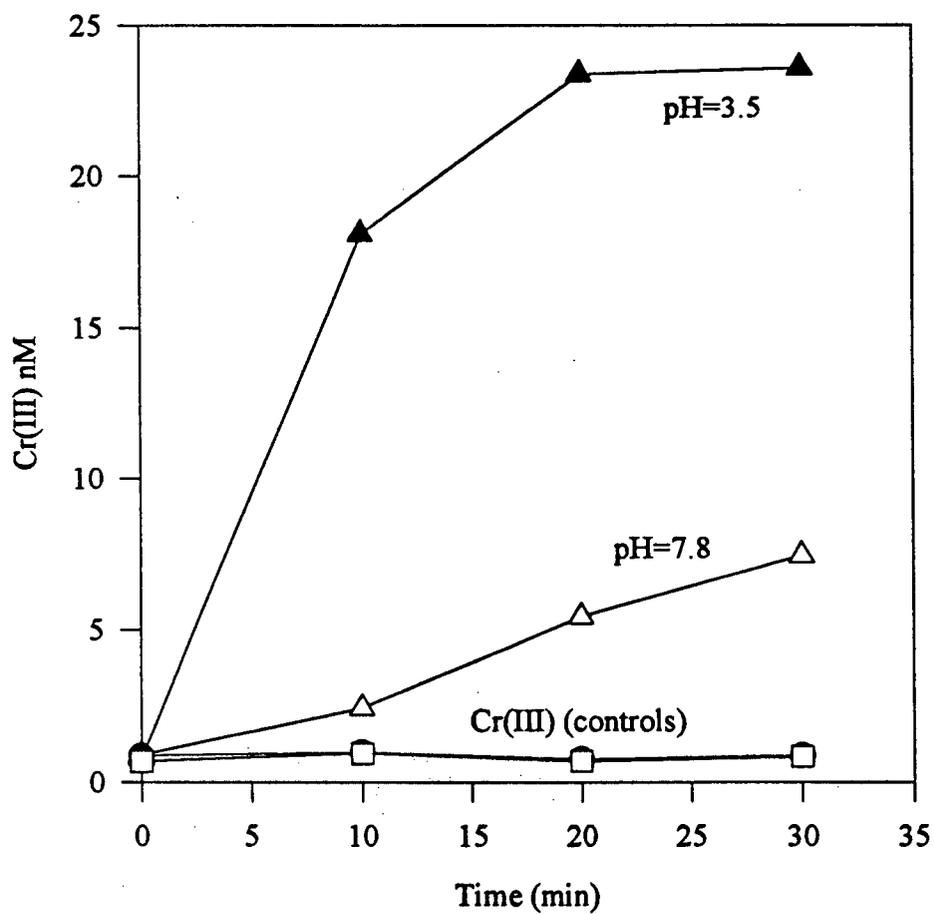


Figure 6.6.1 Reduction of Cr(VI) by Fe(II) as a function of time (min) at pH 3.5 and 7.8, Total Cr = ~ 24 nM, [Fe(II)] = 400 nM, 25 °C.

6.7 IV: Mixing of Oxic and Anoxic Samples

In an attempt to learn more about the process of Cr cycling across the oxic-anoxic interface in Saanich Inlet, a mixing experiment was performed using samples collected in July 1994. The experiment was designed to simulate the mixing of oxic Cr-rich Saanich waters with anoxic waters at the interface or during deep water renewal. One liter of unfiltered oxic Saanich seawater from 110 m depth was mixed with deep anoxic water (1 L, unfiltered) from 200 m in a 2 L Teflon[®] reaction vessel set up in the trace metal clean laminar flow bench. The reaction temperature was maintained at 25 °C with the use of a constant-temperature bath and the mixture stirred continuously with a Teflon[®] coated magnetic stirrer in the capped reaction vessel. At various time intervals after mixing, subsamples were drawn from the reaction vessel and analyzed for labile Cr(III). A few samples were also analyzed for total labile Cr.

6.7.1 Results and Discussion

The concentrations of labile Cr(III), Cr(VI) and total labile Cr at various time intervals (hrs) after the mixing of end-members ($t=0$) are shown in Table 6.7.3.1. Labile Cr(III) decreased rapidly during the first three days, from the initial value of 0.76 nM to 0.16 nM after 170 hrs. After this period labile Cr(III) increased, at a much lower rate, until sample ran out after 29 days. There is insufficient data for a detailed interpretation of the trends for total labile Cr and Cr(VI).

Time (hrs)	Labile Cr(III) (nM)	Cr(VI) (nM)	Total labile Cr (nM)
0	0.76	1.11±0.05	1.87±0.05
10	0.64±0.02		
18	0.37±0.008		
24	0.46	1.20	1.66
48	0.22		
72	0.16±0.02		
168	0.18		
336	0.33		
504	0.37		
720	0.63	1.06	1.69

Table 6.7.3.1 Labile Cr(III), Cr(VI), and total labile Cr concentrations as a function of time in a controlled mixing experiment

It appears as though there are two distinct processes affecting labile Cr(III), one which removes labile Cr(III) from solution and one which releases labile Cr(III) back into solution. Although the experimental setup was somewhat different from the one used here and the timescales for the processes are quite different, a similar trend was seen for Ce and Nd in samples from the Black Sea (Schijf *et al.*, 1994). Ce and Nd decreased to minimum concentrations at 150 min, then increased at a much lower rate until the end of the experiment. A plot of the natural logarithm of labile Cr(III) as a function of time is shown in Figure 6.7.3.1. It appears that labile Cr(III) data in the time intervals 0-170 hrs and 170-720 hrs obey pseudo first-order kinetics with a rate law given by:

$$[\text{Cr}]/[\text{Cr}]_t = \exp(kt) \quad \text{Equation 8}$$

where $[\text{Cr}]$ is the concentration of labile Cr(III) at $t = 0$, $[\text{Cr}]_t$ is the labile Cr(III) concentration at time t , k is the pseudo first-order rate constant, expressed as $-k_1$ and k_2 for the removal and release reactions, respectively. Values for k_1 and k_2 determined from Figure 6.7.3.1 are $-2.15 \times 10^{-2}/\text{hr}^{-1}$ and $2.09 \times 10^{-3}/\text{hr}^{-1}$, respectively.

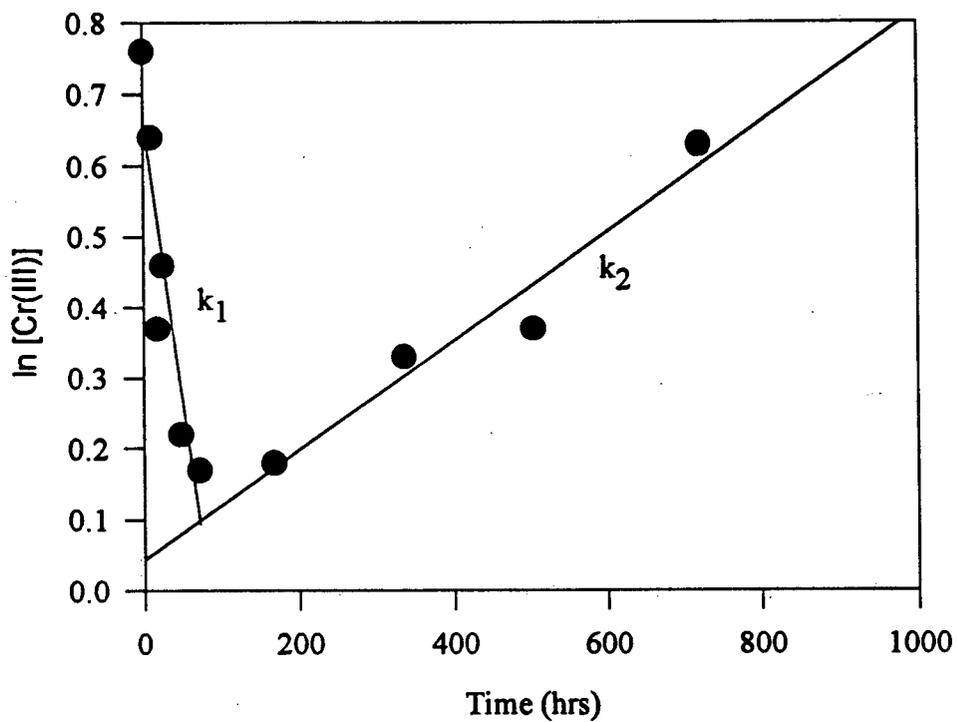


Figure 6.7.3.1 Plots of the natural logarithm of Cr(III) concentrations as a function of time after mixing of Saanich inlet oxic and anoxic samples. Pseudo-first order rate constants, k_1 and k_2 are explained in text.

Several factors such as the presence of Mn and Fe oxyhydroxides, dissolved organic matter and microbial processes can influence the observed Cr(III) trends. Since these samples were not filtered, they contained a substantial amount of particles and dissolved organic matter, both of which could assist in removing labile Cr(III) from solution through sorption and/or coprecipitation. In addition to removal via sorption processes, labile Cr(III) may have been removed via oxidation to the more soluble Cr(VI). After 24 hrs, 0.3 nM (~ 40%) of the original labile Cr(III) was removed, but Cr(VI) increased by only 0.09 nM (~ 8%), thus a decrease in total labile Cr also occurred, probably due to formation of non-labile Cr forms or sorption to bottle walls. The oxidation of Cr(III) is reported to be a slow process due to the kinetic inertness of Cr(III) (Schroeder and Lee, 1975). From the labile Cr(III) removal plot (k_1), a half-life of ~ 30 hrs is obtained. A residence time for Cr(III) in Saanich inlet of 1-4400 days was reported for various depth intervals by Cranston (1979).

During the period of labile Cr(III) release (k_2), labile Cr(III) increased by ~ 200%, in one month, from its lowest value. Determination of Cr(VI) when labile Cr(III) was at a minimum was not done, but the Cr(VI) concentration after 1 month showed a decrease of ~ 11% from the value seen after 24 hrs; during the same period, labile Cr(III) increased by ~ 46 % suggesting that there was a source of labile Cr(III) in addition to reduction of Cr(VI). The data for labile Cr(III) release yields a half-life of ~ 2 weeks, an order of magnitude higher than that for labile Cr(III) removal. Clearly a much slower process is involved in labile Cr(III) release compared to its removal. The release of labile Cr(III) is likely due to reduction of Cr(VI) and/or dissolution of particles onto which Cr(III) was initially sorbed. Schifj *et al.* (1994) observed that the release of Ce and Nd was inhibited in the presence of formaldehyde, suggesting that the release was mediated by Mn and Fe reducing bacteria which had been introduced with the unfiltered seawater. These interpretations, at the moment, represent an educated guess of possible processes that can affect Cr species at the redox interface of Saanich Inlet. More experiments involving both different end-member proportions and also measurements of both Mn and Fe (dissolved and

particulate), dissolved organic matter as well as monitoring changes in redox conditions will be needed to fully address this issue.

6.8 Relevance of Studies to Environmental Conditions

Laboratory studies of Cr species interactions with humic acid have shown that these organic complexes are capable of reducing Cr(VI) under a wide variety of acidic conditions. These results also show that Cr(III) can bind to humic acids resulting in stable, soluble, organic complexes. These findings may have important implications for the aquatic cycle of Cr. In a kinetic study of Cr(III) oxidation by Mn oxides, Johnson *et al.* (1991) observed that Cr(III) bound by salicylic acid was less susceptible to oxidation than unbound Cr. Since Mn oxides are considered to be the most important oxidants for Cr(III) in terrestrial and aquatic systems, reduction of Cr(VI) followed by Cr(III) binding by DOM may be one way in which high Cr(III) values in excess of thermodynamic equilibrium can be maintained, even in areas with high concentrations of Mn oxides such as nearshore and surface waters.

Field observations in Saanich inlet (Chapter 4) revealed that during the stratified summer months, approximately 45-55 % of the Cr in deep anoxic samples was non-labile (detected only after sample oxidation with H₂O₂ and irradiation with UV light). Thus this fraction of Cr was likely bound as dissolved organochromium species by DOM. Laboratory studies are therefore in agreement with field observations on Cr(III) binding to organic matter. The dependence of Cr(VI) reduction on pH suggests that these processes may be more important in reducing, acidic environments. Reduction of Cr(VI) by Fe(II), unlike with HA, was also observed at higher, environmentally relevant pH values. Reduction of mobile and toxic Cr(VI) by organic constituents and Fe(II) to the less harmful and insoluble Cr(III) is an important process in remediation of Cr(VI)-contaminated sites (e.g., Elovitz and Fish, 1994; Makos and Hrnčir, 1995). The relative importance of Cr(VI) reduction by DOM, Fe(II) or other reductants (e.g., hydrogen sulfide, microbes, etc.) will depend on a variety of chemical and environmental factors. In this study, for example, with approximately the same conditions employed, Fe(II) appears to be the faster Cr(VI) reductant than HA particularly at higher pH, typical of environmental conditions. Eary and Rai (1989) also observed instantaneous reduction of Cr(VI) by Fe(II) when the latter was used solely as the reductant. However, when the Fe(II) source was in mineral form (such as

hematite and biotite), the reduction rate was dependent on the dissolution rate of Fe(II) from the minerals. The dissolution rate was observed to increase at lower pH and in the presence of high concentrations of anions that can complex Fe(II) (Eary and Rai, 1989). Various factors can also influence the reduction of Cr(VI) by humic acid. The presence of Cr(III) was shown to slightly inhibit the rate of Cr(VI) reduction by soil humic acids whereas ferric ions increased the rate, even when only a small amount was added (Wittbrodt and Palmer, 1996). Thus chromate reduction by HA, Fe(II) or any other reductant will be regulated by a combination of various environmental factors.

6.9 Summary and Conclusions

Humic acids were shown to be capable of reducing Cr(VI) in aqueous solution under a wide range of acidic pH conditions. The reduction follows a general rate law of the form - $d[\text{Cr(VI)}]/dt = k_1[\text{HCrO}_4^-][\text{HA}]$, where $[\text{HCrO}_4^-]$ denotes the total concentration of bichromate, $[\text{HA}]$ is the total concentration of humic acid and k_1 is a function of pH and temperature. Before the mechanism of such a reaction can be established with certainty, more work is required on the nature of radical intermediates and of the concentrations and stability of Cr species intermediates. Although only preliminary results were obtained, Fe(II) appears to be an even faster reductant for Cr(VI) especially at higher pH values typical of the marine environment. Complexation of Cr(III) by DOM appears to be one way in which elevated levels of Cr(III) may be maintained in solution, particularly in coastal regions with higher dissolved organic matter concentrations. Further laboratory studies are needed to address the role of various interactions on the Cr environmental cycle and to assist in the interpretation of field results.

BIBLIOGRAPHY

- Ahern F., Eckert J. M., Payne N. C., and Williams K. L. (1985) Speciation of chromium in seawater. *Anal. Chim. Acta*, **175** 147-151.
- Ajmal M., Nomani A. A., and Ahmad A. (1984) Acute toxicity of chrome electroplating wastes to microorganisms: adsorption of chromate and chromium(VI) on a mixture of clay and sand. *Wat. Air Soil. Pollut.* **23**, 119-127.
- Alvarez-Macho M. P., and Montequi-Martin M. I. (1991) Chromic oxidation of lactic acid in very strong acid media. *Can. J. Chem.* **68**, 29-32.
- Anderson J. J., and Devol A. H. (1973) Deep water renewal in Saanich Inlet, an intermittently anoxic basin. *Estuarine Coastal Mar. Sci.* **1**, 1-10.
- Bacon M. P., Spencer D. W., and Brewer P. G. (1976) $^{210}\text{Pb}/^{226}\text{Ra}$ and $^{210}\text{Po}/^{210}\text{Pb}$ disequilibrium in seawater and suspended particulate matter. *Earth Planet. Sci. Lett.* **31**, 119-128.
- Bacon M. P., and Anderson R. E. (1982) Distribution of thorium isotopes between dissolved and particulate forms in the deep sea. *J. Geophys. Res.* **87**, 2045-2056.
- Baes C. F., and Mesmer R. E. (1976) In *The Hydrolysis of Cations*. Wiley, New York.
- Balistrieli L. S., Murray J. W., and Paul B. (1992a) The cycling of iron and manganese in the water column of lake Sammamish, Washington. *Limnol Oceanogr.* **37**, 510-528.
- Balistrieli L. S., Murray J. W., and Paul B. (1992b) The biogeochemical cycling of trace metals in the water column of Lake Sammamish, Washington: Response to seasonally anoxic conditions. *Limnol. Oceanogr.* **37**, 529-548.
- Balistrieli L. S., Murray J. W., and Paul B. (1994) The biogenic cycling of trace elements in a biogenic meromictic lake. *Geochim. Cosmochim. Acta* **58**, 3993-4008.
- Barlett R., and James B. (1979) Behaviour of chromium in soils. III. Oxidation. *J. Envir. Qual.* **8**, 31-35.
- Barlett R., and Kimble J. M. (1976) Behaviour of chromium in soils. I. Trivalent forms. *J. Envir. Qual.* **5**, 370-383.
- Benes P., and Steinnes E. (1975) Migration forms of trace elements in natural fresh waters and the effect of the water storage. *Wat. Res.* **9**, 741-749.
- Benoit D. A. (1976) Toxic effects of hexavalent chromium on brook trout (*salvenilus fontinalis*) and rainbow trout (*salmo gairdneri*). *Wat. Res.* **10**, 497-500.

- Bjornsen P. K. (1988) Phytoplankton exudation of organic matter: Why do healthy cells do it? *Limnol. Oceanogr.* **33**, 151-154.
- Black Sea Oceanography: Results from the 1988 Black Sea Expedition* (1991) (ed. J. W. Murray), Pergamon Press, Oxford.
- Bostrom K., and Peterson M. N. A. (1969) The origin of aluminum-ferromanganon sediments in areas of high heat flow on the East Pacific Rise. *Mar. Geol.* **7**, 427-447.
- Bowers T. S., Von Damm K. L., and Edmond J. M. (1985) Chemical evolution of mid-ocean ridge hot springs. *Geochim. Cosmochim. Acta* **49**, 2239-2252.
- Boyle E. A., Sclater F. R., and Edmond J. M. (1977) The distribution of dissolved copper in the Pacific. *Earth Planet. Sci. Lett.* **37**, 38-54.
- Boyle E. A. (1988) Cadmium: chemical tracer of deepwater paleoceanography. *Paleoceanography* **3**, 471-489.
- Bruland K. W. (1983) Trace metal in seawater. In *Chemical Oceanography* (eds. Riley J. P., and Chester R.), pp. 157-220. Academic Press, London.
- Bruland K.W., Knauer G. A., and Martin J. H. (1978) Cadmium in the northeast Pacific waters. *Limnol. Oceanogr.* **23**, 618-625.
- Bruland K.W. (1989) Oceanic zinc speciation: Complexation of zinc by natural organic ligands in the central North Pacific. *Limnol. Oceanogr.* **34**, 267-283.
- Buckley P. J. M., and van den Berg C. M. G. (1986) Copper complexation profiles in the Atlantic Ocean. *Mar. Chem.* **19**, 281-296.
- Buffle J., De Vitre R. R., Perret D., and Leppard G. G. (1989) Physico-chemical characteristics of a colloid iron phosphate species formed at the oxic-anoxic interface of a eutrophic lake. *Geochim. Coschim. Acta* **53**, 399-408.
- Burns R. G. (1970) In *Mineralogical Applications of Crystal Field Theory*. pp. 224. University Press, London.
- Burns V. M., and Burns R. G. (1975) Mineralogy of chromium. *Geochim. Cosmochim. Acta* **39**, 903-910.
- Burton J. D., Statham P. J. (1982) Occurrence, distribution and chemical speciation of some minor dissolved constituents in ocean waters. In *Environmental Chemistry*, Specialist Periodical Report, Royal Society of Chemistry, London. 234-265.

- Campbell J. A., and Yeats P. A. (1981) Dissolved chromium in the northwest Atlantic Ocean. *Earth. Planet. Sci. Lett.* **53**, 427-433.
- Cappuzo J. M., and Anderson F.E. (1973) The use of modern chromium accumulations to determine estuarine sedimentation rates. *Mar. Geol.* **14**, 225-235.
- Carpenter J. H. (1965) The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. *Limnol. Oceanogr.* **37**, 529-548.
- Caspers H. (1957). Black Sea and Sea of Azov. In *Treatise on Marine Ecology and Paleocology* (ed. Hedgpeth J. W.), Geological Society of America Memoire 67 **1**, 801-890.
- Catts J. G., and Langmuir D. (1986) Adsorption of Cu, Pb and Zn by δ -MnO₂: Applicability of the site binding surface complexation model. *Appl. Geochem.* **1**, 255-264.
- Chase R. L., Delaney J. R., Karsten J. L., Johnson H. P., Juniper S. K., Lupton J. E., Scott S. D., Tunnicliffe V., Hammond S. R., and McDuff R. E. (1985) Hydrothermal vents on an axis seamount of the Juan de Fuca Ridge. *Nature* **313**, 212-214.
- Chester R., Aston S. R., and Bruty D. (1976) The trace element partition geochemistry in an ancient deep sea sediment core from the Bermuda Rise. *Mar. Geol.* **21**, 271-288.
- Chester R. (1986) The marine mineral aerosol. In *The Role of Air-Sea Exchange in Geochemical Cycling* (ed. Buart-Menard P.), pp. 443-476. Reidel, New York.
- Coale K. H., and Bruland K. W. (1985) ²³⁴Th: ²³⁸U disequilibria within the California current. *Limnol. Oceanogr.* **23**, 618-625.
- Collienne R. H. (1983) Photoreduction of iron in the epilimnion of acidic lakes. *Limnol. Oceanogr.* **28**, 83-100.
- Connett P. H., and Wetterhahn K. E. (1985) In vitro reaction of the carcinogen chromate (VI) with cellular thiols and carboxylic acids. *J. Am. Chem. Soc.* **107**(14), 4282-4288.
- Connett P. H., and Wetterhahn K. E. (1986) Reactions of chromium(VI) with thiols: pH dependence of Cr(VI) thio ester formation. *J. Am. Chem. Soc.* **108**, 1842-1847.
- Craig H. (1974) A scavenging model for trace elements in the deep sea. *Earth Planet. Sci. Lett.* **23**, 5491-5506.
- Cranston R. E., and Murray J. W. (1978) The determination of chromium species in natural waters. *Anal. Chim. Acta* **99**, 275-282.
- Cranston R. E., and Murray J. W. (1980) Chromium species in the Columbia River and estuary. *Limnol. Oceanogr.* **25**, 1104-1112.

- Cranston R. E. (1979) Chromium species in natural waters. Ph.D. dissertation, pp. 222-243. University of Washington, Seattle.
- Cranston R. E. (1983) Chromium in Cascadia Basin, Northeast Pacific Ocean. *Mar. Chem.* **13**, 109-125.
- Cutter G. A. (1982) Selenium in reducing waters. *Science* **217**, 829-831.
- Davis J. A., and Leckie J. O. (1978) Surface ionization and complexation at the oxide /water interface. 2. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *J. Colloid Interface Sci.* **67**, 90-105.
- Davison W., and Tipping E. (1984) Treading in Mortimer's footsteps: The geochemical cycling of iron and manganese in Esthwaite water. *Freshwater Biol. Assoc. Annu. Rep.* **52**, 91-101.
- Davison W., and Seed G. (1983) The kinetics of the oxidation of ferrous iron in synthetic and natural waters. *Geochim. Coschim. Acta* **47**, 67-79.
- Davison W. (1981) Supply of iron and manganese to an anoxic basin. *Nature* **290**, 241-243.
- Davison W. (1985) Conceptual model for transport at a redox boundary. In *Chemical Processes in Lakes* (ed. Stumm W.), pp. 31-53. Wiley, New York.
- Davison W. (1993) Iron and manganese in lakes. *Earth-Science Rev.* **34**, 119-163.
- Delaney J. R., Johnson H. P., and Karsten J. L. (1981) The Juan de Fuca Ridge-Hot Spot-Propagating Rift System: new tectonic, geochemical, and magnetic data. *J. Geophys. Res.* **86**, 11747-11750.
- De Vitre R. R., Buffle J., Perrret D., and Baudat R. (1988) A study of iron and manganese transformations at the O₂/S(-II) transition layer in a eutrophic lake (Lake Bret, Switzerland): A multimethod approach. *Geochim. Cosmochim. Acta* **52**, 1601-1613.
- Devol A. H. (1975) Biological oxidations in oxic and anoxic marine environments: rates and processes. Ph.D. Thesis, pp 208. University of Washington, Seattle.
- Diem D., and Stumm W. (1984) Is dissolved Mn⁺² being oxidised by O₂ in absence of Mn-bacteria or surface catalysts? *Geochim. Cosmochim. Acta* **48**, 1571-1573.
- Donat J. R., and van den Berg C. M. G. (1992) A new cathodic stripping voltammetric method for determining organic copper complexation in seawater. *Mar. Chem.* **38**, 69-90.
- Donat J. R., and Bruland K. W. (1995) Trace elements in the oceans. In *Trace Elements in Natural Waters* (ed. Steinnes and Salbu), pp. 247-280. CRC Press, Boca Raton.

- Douglas G. S., Mills G. L., and Quinn J. G. (1986) Organic copper and chromium complexes in the interstitial waters of Narragansett Bay sediments. *Mar. Chem.* **19**, 161-174.
- Dulka J. J., and Risby T. H. (1976) Ultratrace metals in some environmental and biological systems. *Anal. Chem.* **48**, 640A-653A.
- Dymond J., Corliss J. B., Heath R., Field W. C., Dasch E. J., and Veeh H. H. (1973) Origin of metalliferous sediments from the Pacific Ocean. *Geol. Soc. Am. Bull.* **84**, 3355-3372.
- Early J. E., and Cannon R. D. (1965) Aqueous Chemistry of Chromium(III). In *Transition Metal Chemistry Vol. 1*, Marcel Dekker, Inc., New York.
- Eary L. E., and Rai D. (1987) Kinetics of chromium(III) oxidation to Cr(VI) by reaction with manganese dioxide. *Envir. Sci. Technol.* **22**, 697-702.
- Eary L. E., and Rai D. (1988) Chromate removal from aqueous wastes by reduction with ferrous ions. *Environ. Sci. Technol.* **22**, 972-977.
- Eary L. E., and Rai D. (1989) Kinetics of chromate reduction by ferrous ions derived from hematite and biotite at 25 °C. *Am J. Sci.* **289**, 180-213.
- Eckert J. M., Stewart J. J., Waite T. D., Szymzak R., and Williams K. L. (1990) Reduction of chromium (VI) at sub- $\mu\text{g L}^{-1}$ levels by fulvic acid. *Anal. Chim. Acta* **236**, 357-362.
- Edmond J. M., Measures C. I., Mangum B., Grant B., Sclater F. R., Collier R., Hudson A., Gordon L. I., and Corliss J. B. (1979) On the formation of metal-rich deposits at ridge crests. *Earth Planet. Sci. Lett.* **9**, 10-16.
- Edmond J. M., Von Damm K. L., McDuff R. E., and Measures C. I. (1982) Chemistry of hot springs on the East Pacific Rise and their effluent dispersa. *Nature* **297**, 187-191.
- Edmond J. M., Measures C. I., McDuff R. E., Chan L., Collier R., Grant Gordon L. I., and Corliss J. B. (1979) Ridge crest hydrothermal activity and the balances of the major and minor elements in the oceans: The Galapagos data. *Earth Planet. Sci. Lett.* **46**, 1-18.
- Elderfield H. (1970) Chromium speciation in seawater. *Earth Planet. Sci. Lett.* **9**, 10-16.
- Elovitz M. S., and Fish W. (1994) Redox Interactions of Cr(VI) and substituted phenols: kinetic investigation. *Environ. Sci. Technol.* **28**, 2161-2169.
- Emerson S., Kalhorn S., Jacobs L., Tebo B. M., Neelson K. H., and Rosson R. A. (1982) Environmental oxidation rate of manganese(II): bacterial catalysis. *Geochim. Cosmochim. Acta* **46**, 1073-1079.

- Emerson S., Jacobs L., and Tebo B. M. (1983). The behavior of trace metals in marine anoxic waters: solubilities at the oxygen-hydrogen sulphide interface. In *Trace Metals in Seawater* (eds. Wong C.S., Boyle E., Bruland K. W., Burton J. D and Goldberg E. D.), pp. 579-608. Plenum Press, New York.
- Emerson S., Cranston R. E., and Liss P. S. (1979) Redox species in a reducing fjord: equilibrium and kinetic considerations. *Deep-Sea Res.* **26**, 859-873.
- Fay R. C., and Piper T. S. (1963) Coordination compounds of trivalent metals with unsymmetrical bidentate ligands. II. Trifluoroacetylacetonates. *J. Am. Chem. Soc.* **85**, 500-504.
- Feely R. A., Massoth G. J., Trefry J. H., Baker E. T., Paulson A. J., and Lebon G. T. (1994) Composition and sedimentation of hydrothermal plume particles from North Cleft Segment, Juan de Fuca Ridge. *J. Geophys. Res.* **99**, 4985-5006.
- Fluorie E. J. (1972) Particulate manganese in seawater stressing regimes in marine anoxic basins. Ph.D. Thesis, pp. 138. University of Washington.
- Forstner U., and Wittman G. T. W. (1979) *Metal Pollution in the Aquatic Environment*. Springer, Berlin.
- Forstner U. (1982) Accumulative phases for heavy metals in limnic sediments. *Hydrobiol.* **91**, 269-284.
- Froelich P. N., Klinkhammer G. P., Bender L. M., Luedtke N. A., Heath G. R., Cullen D., and Dauphin P. (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta* **43**, 1075-1090.
- Gaillard J. F., Jeandel C., Michard G., Nicolas E., and Renard E. (1986) Interstitial water chemistry of Villefranche Bay sediments: Trace metal diagenesis. *Mar. Chem.* **18**, 233-247.
- Gjessing E. T. (1976) Physical and chemical characteristics of Aquatic humus. Ann Arbor Science, Ann Arbor, MI.
- Graham G. T. E., and Westheimer F. H. (1958) The kinetics of the chromic acid oxidation of benzaldehyde. *J. Am. Chem. Soc.* **80**, 3030-3033.
- Green W. J., Ferdelman T. G., and Canfield D. E. (1989) Metal dynamics in lake Vanda (Wright Valley, Antarctica). *Chem. Geol.* **76**, 85-94.
- Gupta S. K. K., Samanta T., and Basu S. N. (1986) Kinetics and mechanism of oxidation of ethanol, isopropanol and benzyl alcohol by chromium(VI) in perchloric acid medium. *Tetrahedron* **42**, 681-685.

- Guptu S. K., Chen K. Y. (1975) Partitioning of trace metals in selective chemical fractions of nearshore sediments. *Envir. Lett.* **10**, 129-158.
- Gupta S. K. K., Dey S., and Gupta S. S. (1990) Evidence of esterification during the oxidation of some aromatic aldehydes by chromium(VI) in acid medium and the mechanism of the oxidation process. *Tetrahedron* **46**, 2431-2444.
- Hart B. T. (1982) Uptake of trace metals by sediments and suspended particulates: a review. *Hydrobiol.* **91**, 299-313.
- Harvey G. R., Boran D. A., Chesal L. A., and Tokar J. M. (1983) The structure of marine fulvic and humic acids. *Mar. Chem.* **12**, 119-132.
- Herlinveaux R. H. (1962) Oceanography features of Saanich Inlet: 9 May-2 July 1966. *Fish. Res. Bd. Canada Tech. Rep. no. 300*.
- Herlinveaux R. H. (1962) Oceanography of Saanich Inlet in Vancouver Island, British Columbia. *J. Fish. Res. Bd. Canada* **19**, 1-37.
- Herlinveaux R. H. (1972) Features of water movement over the sill of Saanich Inlet: June-July 1966. *Fish. Res. Bd. Canada Tech. Rep. no. 99*.
- Hoffert M., Person M., Courtois C., Karpoff A. M., and Trauth D. (1980) Sedimentology, mineralogy, and geochemistry of hydrothermal deposits from holes 424, 424A, 424B, 424C (Galapagos spreading center). Initial Reports DSDP 54, 339-376.
- Hunt J. P. (1963) In *Metal Ions in Aqueous Solution*. Benjamin Inc., New York.
- Irvine T. N. (1975) Crystallization sequences in the muskox intrusion and other layered intrusions. II. Origin of chromite layers and similar deposits of other magmatic ores. *Geochim. Cosmochim. Acta* **39**, 991-1020.
- Jacobs L., and Emerson S. (1982) Trace metal solubility in an anoxic fjord. *Earth Planet. Sci. Lett.* **60**, 237-252.
- Jacobs L., Emerson S., and Skei J. (1985) Partitioning and transport of metals across the O₂/H₂S interface in a permanently anoxic basin: Framvarenn Fjord, Norway. *Geochim. Cosmochim. Acta* **49**, 1433-1444.
- Jacobs L., Emerson S., and Husted S. S. (1987) Trace metal geochemistry in the Cariaco Trench. *Deep-Sea Res.* **34**, 965-981.
- James B. R., and Bartlett R. J. (1983) Behaviour of chromium in soils. VII. Adsorption and reduction of hexavalent forms. *J. Envir. Qual.* **12**, 177-181.

- Jeandel C., and Minster J. F. (1984) Isotope dilution measurement of inorganic chromium(III) and total chromium in seawater. *Mar. Chem.* **14**, 347-364.
- Jeandel C., and Minster J. F. (1987) Chromium behaviour in the ocean: Global versus regional processes. *Global Biogeochem. Cycles* **1**, 131-154.
- Johnson C. A., Sigg, L., and Lindauer U. (1992) The chromium cycle in a seasonally anoxic lake. *Limnol. Oceanogr.* **36**, 315-321.
- Johnson C. A., Ulrich M., Sigg L., and Imboden D. M. (1991) A mathematical model of the manganese cycle in a seasonally anoxic lake. *Limnol. Oceanogr.* **36**, 1415-1426.
- Johnson C. A., and Xyla A. G. (1991) The oxidation of chromium(III) to Cr(VI) on the surface of manganite (γ -MnOOH). *Geochim. Cosmochim. Acta* **55**, 2861-2866.
- Jones C. J., Johnson H. P., and Delaney J. R. (1981) Distribution of hydrothermal manganese over the Juan de Fuca Ridge. *Geophys. Res. Lett.* **8**, 873-876.
- Jones L. H. P., and Jarvis S. C. (1981) The fate of heavy metals. In *The Chemistry of Soil Processes* (eds. Greenland D. J., and Hayes M. H. B.), pp 593-620. Wiley, New York.
- Jorgensen B. B. (1977) Bacterial sulfate reduction within reduced microniches of oxidized marine sediments. *Mar. Biol.* **41**, 7-17.
- Kaczynski S. E., and Kieber R. J. (1993) Aqueous trivalent chromium photoproduction in natural waters. *Environ. Sci. Technol.* **27**, 1572-1576.
- Kaczynski S. E., and Kieber R. J. (1994) Hydrophobic C18 bound organic complexes of chromium and their potential impact on the geochemistry of chromium in natural waters. *Environ. Sci. Technol.* **28**, 799-804.
- Kastner M. (1981) Authigenic silicates in deep sea sediments: formation and diagenesis. In *The Sea*, vol 7 (ed. Emiliani C. E.), pp. 938-940. Wiley Interscience, New York.
- Kick H., Norsbers R., and Warnusz J. (1971) The availability of Cr, Ni, Zn, Cd, Sn, and Pb for plants. *Proc. Int. Symp. Soil Fertilization Evaluation* **1**, 1039-1045.
- Kieber R. J., and Helz G. R. (1992) Indirect photoreduction of aqueous chromium(VI). *Environ. Sci. Technol.* **29**, 307-312.
- Klinkhammer G. P., and Hudson A. (1986) Dispersal patterns for hydrothermal plumes in the South Pacific using manganese as a tracer. *Earth Planet. Sci Lett.* **79**, 241-249.

- Kopp J. F., and Kroner R. C. (1968) Trace metals in waters of the United States: A five year summary of trace metals in rivers and lakes in the U.S. (1962-1967), pp.256. U.S. Department of the Interior Cincinnati, Ohio.
- Kremling K. (1983) The behavior of Zn, Cd, Cu, Ni, Co, Fe, and Mn in anoxic Baltic waters. *Mar. Chem.* **13**, 87-108.
- Landing W. M., Haroldsson C., and Paxeus N. (1986) Vinyl polymer agglomerate based transition metal cation chelating ion-exchange resin containing the 8-hydroxyquinoline functional group. *Anal. Chem.* **58**, 3031-3035.
- Landing W. M., and Lewis B. L. (1991) Thermodynamic modeling of trace metal speciation in the Black Sea. In *Black Sea Oceanography* (eds. E. Ikdar and J.W Murray), pp.125-160. Kluwer Press.
- Landing W. M., Burnett W. C., Lyons W. B., and Orem W. H. (1991). Nutrient cycling and the biogeochemistry of manganese, iron, and zinc in Jellyfish Lake, Palau. *Limnol. Oceanogr.* **36**, 515-525.
- Landing W. M., and Westerlund S. (1988) The solution chemistry of iron(II) in Framraven Fjord. *Mar. Chem.* **23**, 329-343.
- Landing W. M., and Bruland K. W. (1980) Manganese in the North Pacific. *Earth Planet. Sci. Lett.* **49**, 45-56.
- Langard S., and Norseth T. (1979) In *Handbook on the Toxicology of Metals*. (eds. Friberg L., et al.), pp. 383-397. Elsevier/North-Holland Biomedical Press, Amsterdam.
- Lasaga, A. C. (1981) Transition State Theory In *Kinetics of Geochemical Processes* (eds Lasaga A. C., and Kirkpatrick R. J.), vol 8, pp. 135-169. American Mineralogical Society, Washington, DC.
- Laxen D. P. H. (1984) Adsorption of Cd, Pb, and Cu during the precipitation of hydrous ferric oxide in natural water. *Chem. Geol.* **47**, 321-332.
- Laxen D. P. H. (1985) Trace metal adsorption/coprecipitation on hydrous ferric oxide under realistic conditions. The role of humic substances. *Water Res.* **19**, 1229-1236.
- Laxen D.P.H., and Sholkovitz E. (1985) Adsorption (co-precipitation) of trace metals at natural concentrations on hydrous ferric oxide in lake water samples. *Environ. Technol. Lett.* **2**, 561-568.
- Lee D. G., Stewart R. J. (1967) The oxidation of aliphatic secondary alcohols by chromium(VI) in concentrated sulphuric acid solutions. *J. Org. Chem.* **32**, 2868-2871.
- Lee D. G., and Chen T. J. (1991) Oxidation of organic sulfides by permanganate ion. *J. Org. Chem.* **56**, 5341-5345.

- Lewis B. L., and Landing W. M. (1991) The biogeochemistry of manganese and iron in the Black Sea. *Deep-Sea Res.* **38** (suppl.), S773-S803.
- Linck R. G. (1976) In *Survey of Progress in Chemistry*. (ed. Scott A. F.), Vol. 7, pp. 89. Academic Press, New York.
- Lupton J. E., Delaney J. R., Johnson H. P. and Tivey M. K. (1985) Entrainment and vertical transport of deep ocean water by buoyant hydrothermal plumes. *Nature* **316**, 621-623.
- Martin J. H., and Knauer G. A. (1973) The elemental composition of plankton. *Geochim. Cosmochim. Acta* **37**, 1639-1654.
- Mason B. (1958) In *Principles of Geochemistry*. Wiley, New York.
- Mathur A. K., Chandra S. V., and Tandon S. K. (1977) Comparative toxicity of trivalent and hexavalent chromium to rabbits. *Toxicology* **8**, 53-61.
- Mayer L. M., and Fink L. K. (1980) Granulometric dependence of chromium accumulation in estuarine sediments in Maine. *Estuar. Coast. Mar. Sci.* **11**, 491-503.
- Mayer L. M., Schick L. L., and Chang C. A. (1983) Kinetics of trivalent chromium complexation and adsorption at the river-estuary interface: implications for reactive pollutant transport. *Int. Conf. on Heavy Metals in the Environment* **2**, 1112-1115.
- Mayer L. M., Schick L. L., and Chang C. A. (1983) Incorporation of trivalent chromium into riverine and estuarine colloidal material. *Geochim. Cosmochim. Acta* **48**, 1717-1722.
- Mayer L. M., and Schick L. L. (1981) Removal of hexavalent chromium from estuarine waters by model substrates and natural sediments. *Environ. Sci. Technol.* **15**, 1482-1484.
- McAuley A., and Olatunji M. A. (1977) Metal-ion oxidations in solution. Part XIX. Redox pathways in the oxidation of penicillamine and glutathione by chromium(VI). *Can. J. Chem.* **55**, 3335-3340.
- Measures C. I., and Edmond J. M. (1986) Determination of beryllium in natural waters in real time using electron capture detection gas chromatography. *Anal Chem.* **58**, 2065-2069.
- Measures C. I., and Edmond J. M. (1989) Shipboard determination of aluminum in seawater at the nanomolar level by electron capture detector gas chromatography. *Anal Chem.* **61**, 544-547.
- Measures C. I., and Edmond J. M. (1992) The distribution of aluminum in the Greenland Sea and its relationship to ventilation processes. *J. Geophys. Res.* **97**, 17787-17800

- Mertz W. (1974) Chromium as a dietary essential for man. In *Trace Elements Metabolism* (eds. Hoekstra W. G., Suttie J. W., Ganther K. E., and Mertz W.), Vol. 2, pp. 185-198. University Park Press, Baltimore.
- Mofett J. W., Zika R. G., and Brand L. E. (1990) Distribution and potential sources of copper chelators in the Sargasso Sea. *Deep-Sea Res.* **37**, 27-36.
- Mofett J. W. (1995) The spatial and temporal variability of copper complexation by strong organic ligands in the Sargasso Sea. *Deep-Sea Res.* **42**, 1273-1295.
- Morel F. M. M. (1983) In *Principles of Aquatic Chemistry*. Wiley, New York.
- Morfett K., Davison W., and Hamilton-Taylor J. (1988) Trace metal dynamics in a seasonally anoxic lake. *Environ. Geol. Water Sci.* **11**, 107-117.
- Morgan W. J. (1972) Deep mantle convection plumes and plate motions. *Bull. Am. Pet. Geol.* **56**, 203-213.
- Morgan W. J. (1973) Plate motions and deep mantle convection. In *Studies in Earth and Space Sciences* (Hess Volume) (ed. R. Shagam et al.), *Geol. Soc. Am. Memoir* 132.
- Mugo R. K., and Orians K. J. (1993). Seagoing method for the determination of Cr(III) and total dissolved Cr in Seawater by electron capture detection gas chromatography. *Anal. Chim. Acta.* **271**, 1-9
- Mugo R. K. (1991) The development of a technique for the determination of dissolved Cr(III) and total dissolved Cr in seawater by electron capture detection gas chromatography. MSc. thesis. pp. 101. University of British Columbia, Canada.
- Munk W. (1966) Abyssal recipes. *Deep-Sea Res.* **9**, 707-730.
- Murray J. W. (1987) Mechanisms controlling the distributions of trace elements in oceans and lakes. In *Sources and Fates of Aquatic Pollutants* (eds. Hites R. A., Eisenreich S. J.), pp. 153-184. American Chemical Society.
- Murray J.W., Spell B., and Paul B. (1983) The contrasting geochemistry of manganese and chromium in the Eastern Pacific Ocean. In *Trace Metals in Seawater*. (eds. Wong C. S., Bruland K., Burton J. D., and Goldberg E. D.), pp. 643-670. Plenum Press, New York.
- Nakayama E., Kuwamoto T., Tsurubo S., Tokoro H., and Fujinaga T. (1981a) Chemical speciation of chromium in seawater. Part 1. Effect of naturally occurring organic materials on the complex formation of chromium(III). *Analyt. Chim. Acta* **130**, 289-294.

- Nakayama E., Kuwamoto T., Tsurubo S., Tokoro H., and Fujinaga T. (1981b) Chemical speciation of chromium in seawater. Part 2. Effect of manganese oxides and reducible organic materials on the redox processes of chromium. *Analyt. Chim. Acta* **130**, 401-404.
- Nakayama E., Kuwamoto T., Tsurubo S., Tokoro H., and Fujinaga T. (1981c) Chemical speciation of chromium in seawater. Part 3. The determination of Cr species. *Anal. Chim. Acta* **131**, 247-254.
- National Research Council of Canada (1976) Effects of Cr in the Canadian Environment. Publication no. 15017, pp. 168. NRCC, Ottawa, Canada.
- Nieboer E., and Jusys A. A. (1988) In *Chromium in the Natural and Human Environments*. (eds. Nriagu J. O., Nieboer E.), Advances in Environmental Science and Technology. Vol. 20, pp. 21-80. Wiley-Interscience, New York.
- Nimmo M., van den Berg C. M. G., and Brown J. (1989) The chemical speciation of dissolved nickel, copper, vanadium, and iron in Liverpool Bay, Irish Sea. *Estuarine Coastal Shelf Sci.* **29**, 57-74.
- Osaki S., Osaki T., Setoyama M., and Takashima Y. (1983) Gel chromatographic behaviour of trace amounts of chromiium(VI) and Chromium(III) in aqueous solution. *J. Chromatogr.* **257**, 180-184.
- Pedersen T. F., Mueller B., McNee J. J., and Pelletier C. A. (1993) The early diagenesis of submerged sulfide-rich tailings in Anderson Lake, Manitoba. *Can. J. Earth Sci.* **30**, 1099-1109.
- Pettine M., and Millero F. J. (1990) Chromium speciation in seawater: the probable role of hydrogen peroxide. *Limnol. Oceanogr.* **35**, 730-736.
- Pettine M., and Millero F. J. (1991) Chromium(III) interactions in seawater through its oxidation kinetics. *Mar. Chem.* **34**, 29-46.
- Pettine M., Millero F. J., and Passino R. (1994) Reduction of chromium(VI) with hydrogen sulfide in NaCl media. *Mar. Chem.* **46**, 335-344.
- Rai D., Zachara J. M., Eary L. E., Girvin D. C., Moore D. A., Resch C. T., Sass B. M., and Schmidt R. L. (1986). Geochemical behaviour of chromium species. Electric Power Research Institute Report EA-4544. Palo Alto, California.
- Rai D., and Zachara J. M. (1988) Chromium reactions in geologic materials. Electric Power Research Institute Report EA-5741. Palo Alto, California.
- Rai D., Sass B. M., and Moore D. A. (1987) Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide. *Inorg. Chem.* **26**, 345-349.

- Rai D., Eary L. E., and Zachara J. M. (1989) Environmental chemistry of chromium. *Sci. Tot. Env.* **86**, 15-23.
- Richard F.C., and Bourg A. C. M. (1991) Aqueous geochemistry of chromium: a review. *Wat. Res.* **25**(7), 807-816.
- Robertson F. N. (1975) Hexavalent chromium in the groundwater in Paradise Valley, Arizona. *Groundwater* **13**, 516-527.
- Rollinson C. L. (1973) Chromium, molybdenum, and tungsten. In *Comprehensive Inorganic Chemistry*. (ed. Bailar J. C. Jr., Emeleus H. J., Nyholm R., and Trotman-Dickenson A. F.), Volume 3, chapter 36, pp. 623-700. Pergamon Press, Oxford.
- Ross D. S., Sjorgen R. E., and Bartlett R. J. (1981) Behaviour of chromium in soils. IV. Toxicity to microorganisms. *J. Environ. Qual.* **10**, 145-148.
- Rosson R. A., Tebo B. M., and Nealson K. H. (1984) Use of poisons in the determination of microbial manganese binding rates in seawater. *Appl. Envir. Microbiol.* **47**, 740-745.
- Rue E. L., Smith G. J., Cutter G. A., and Bruland K. W. (1996) The response of trace element redox couples to suboxic conditions in the water column. *Deep-Sea Res.* (in press).
- Saleh F. Y., Parkerton T. F., Lewis R. V., Huang J. H., and Dickson K. L. (1989) Kinetics of chromium transformations in the environment. *Sci. Tot. Envir.* **86**, 25-41.
- Salomons W., and De Groot A. J. (1978) Pollution history of trace metals in sediments as affected by the Rhine river. In *Environmental Biogeochemistry* (ed. Krumbein W. E.), pp. 149-162. Ann Arbor Science, Ann Arbor, Michigan.
- Santschi P. H. (1988) Factors controlling the biogeochemical cycles of trace elements in coastal marine waters as revealed by artificial radioisotopes. *Limnol. Oceanogr.* **33**, 848-866.
- Sass B. M., and Rai D. (1987) Solubility of amorphous chromium(III)-iron(III) hydroxide solid solutions. *Inorg. Chem.* **26**, 2228-2232.
- Saxby J. D. (1969) Metal-organic chemistry of the geochemical cycle. *Rev. Pure and Appl. Chem.* **19**, 131-150.
- Schaule B. K., and Patterson C. C. (1981) Lead concentration in the Northeast Pacific: evidence for global anthropogenic perturbations. *Earth Planet. Sci. Lett.* **54**, 97.
- Schijf J., De Barr H. J. W., Wijbrans J. R., and Landing W. M. (1991) Dissolved rare earth elements in the Black Sea. *Deep-Sea Res.* **38** (Suppl.), S805-S823.

- Schijf J., De Barr H. J. W., and Millero F. J. (1994) Kinetics of Ce and Nd scavenging in Black Sea waters. *Mar. Chem.* **46**, 345-359.
- Schroeder D. C., and Lee G. F. (1975). Potential transformations of chromium in natural waters. *Water Air Soil Pollut.* **4**, 355-365.
- Selli E., De Giorgia A., and Bidoglio G. (1996). Humic acid-sensitized photoreduction of Cr(VI) on ZnO particles. *Environ. Sci. Technol.* **30**, 598-604.
- Seyler P., and Martin J. (1989) Biogeochemical processes affecting arsenic species distribution in a permanently stratified lake. *Environ. Sci. Technol.* **23**, 1258-1263.
- Sherrell R. M., and Boyle E. A. (1988) Zinc, chromium, vanadium and iron in the Mediterranean Sea. *Deep-Sea Res.* **35**, 1319-1334.
- Sholkovitz E. R., and Copeland D. (1982) The chemistry of suspended matter in Esthwaite Water, a biologically productive lake with seasonally anoxic hypolimnion. *Geochim. Cosmochim. Acta.* **46**, 393-410.
- Sigg L., Johnson C. A., and Kuhn A. (1991) Redox conditions and alkalinity generation in a seasonally anoxic lake (Greiffen). *Mar. Chem.* **36**, 9-26.
- Sigg L. (1985) Metal transfer mechanisms in lakes: the role of settling particles. In: *Chemical Processes in Lakes*. (ed. Stumm W.), pp. 283-310. Wiley, New York.
- Smillie R. H., Hunter K., and Loutit M. (1981) Reduction of chromium(VI) by bacterially produced hydrogen sulfide in a marine environment. *Wat. Res.* **15**, 1351-1354.
- Sorokim Y. I. (1983) The Black Sea. In *Ecosystems of the World 26: Estuaries and Enclosed Sea*. (ed. Ketchum B. H.), pp. 253-292. Elsevier, Amsterdam.
- Spencer D. W., Brewer P. G. and Sachs P. L. (1971) Aspects of the distribution and trace element composition of suspended matter in the Black Sea. *Geochim. Cosmochim. Acta* **36**, 71-86.
- Spencer D. W. and Brewer P. G. (1971) Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. *J. Geophys. Res.* **76**, 5877-5892.
- Spokes L. J., and Liss P. S. (1996) Photochemically induced redox reaction in seawater. 1. Cations. *Mar. Chem.* **49**, 201-213.
- Strubican V. S., and Greskovich C. (1975) Trivalent and divalent chromium ions in spinels. *Geochim. Cosmochim. Acta* **39**, 575-881.

- Sunda W. G., Hunstman S. A., and Harvey G. R. (1983) Photoreduction of manganese oxides in seawater and its geochemical and biological implications. *Nature* **301**, 234-236.
- Sunda W. G., and Hunstman S. A. (1994) Photoreduction of manganese oxides in seawater. *Mar. Chem.* **46**, 133-152.
- Szilagyi M. (1971) Reduction of Fe^{3+} ions by a humic acid preparation. *Soil Sci.* **111**, 233-235.
- Taube H. (1970) In *Electron Transfer Reactions of Complex Ions in Solution*. Academic Press, New York.
- Tebo B. M., Nealson K. H., Emerson S., and Jacobs L. (1984) Microbial mediation of Mn(II) and Co(II) precipitation at the $\text{O}_2/\text{H}_2\text{S}$ interfaces in two anoxic fjords. *Limnol. Oceanogr.* **29**, 1247-1258.
- Tebo B. M., and Emerson S. (1985) Effect of oxygen tension, Mn(II) concentration, and temperature on the microbially catalyzed Mn(II) oxidation rate in a marine fjord. *Appl. Environ. Microbiol.* **50**, 1268-1273.
- Tebo B. M., and Emerson S. (1986) Microbial manganese(II) oxidation in the marine environment: a quantitative study. *Biogeochemistry* **2**, 149-161.
- Tebo B. M., Taylor C. D., Nealson K. H., and Emerson S. (1985) In situ manganese(II) binding rates at the oxic/anoxic interface in Saanich Inlet, B.C., Canada. In: *Planetary Ecology* (eds. Caldwell D. E., Brierley J. A., and Brierley C. L.), pp. 210-221. Van Nostrand Reinhold Co., New York.
- Tebo B. M. (1991) Manganese(II) oxidation in the suboxic zone of the Black Sea. *Deep-Sea Res.* **38** (Suppl.), S883-S905.
- Tessier A. (1992) Sorption of trace elements on natural particles in oxic environments. In *Environmental Particles*. (eds. Buffle J., Van Leeuwen H. P.), Vol 1, pp. 425-453. Lewis, Boca Raton.
- Tipping E., Thompson D. W., and Davison W. (1984) Oxidation products of Mn(II) in lakes. *Chem. Geol.* **44**, 359-383.
- Tipping E., and Heaton M. J. (1983) The adsorption of aquatic humic substances by two oxides of manganese. *Geochim. Coschim. Acta* **47**, 1393-1397.
- Tipping E., and Ohnstad M. (1984) Colloid stability of iron oxide particles from a freshwater lake. *Nature* **308**, 266-268.
- Tolmazin D. (1985) Changing coastal oceanography in the Black Sea. 1. northwestern shelf. *Prog. in Oceanogr.* **15**, 217-276.

- Trocine R. P. T., and Trefry J. H. (1988) Distribution and chemistry of suspended particles from an active hydrothermal vent site on the Mid-Atlantic Ridge at 26 °N. *Earth Planet. Sci. Lett.* **88**, 1-15.
- Tsunogai S. (1971) Iodine in the deep water of the ocean. *Deep-Sea Res.* **18**, 913-919.
- Van den Berg C. M. G., Boussemart M., Kuniyiko Y., Prartono T., and Campos L. A. M. (1994) Speciation of aluminum, chromium and titanium in the NW Mediterranean. *Mar. Chem.* **45**, 267-282.
- Van den Berg C. M. G. (1984) Determination of the complexing capacity and conditional stability constants of complexes of copper (II) with natural organic ligands in seawater by stripping cathodic voltammetry of copper-catechol complex ions. *Mar. Chem.* **15**, 1-15.
- Van den Berg C. M. G., and Nimmo M. (1987) Determination of interactions of nickel with dissolved organic material in seawater using cathodic stripping voltammetry. *Sci. Tot. Environ.* **60**, 185-195.
- Van Der Weijden C. H., Middleburg J. J., De Lange G. J., Van Der Sloot H. A., Hoede D., and Woittiez J. R. W. (1990) Profiles of redox-sensitive trace elements As, Sb, V, Mo, and U in the Tyro and Bannock basins (eastern Mediterranean). *Mar. Chem.* **31**, 171-186.
- Vogt P. R., and Johnson G. L. (1973) Magnetic telechemistry of oceanic crust? *Nature* **245**, 373-375.
- Vogt P. R., and Byerly G. R. (1976) Magnetic anomalies and basalt composition in the Juan de Fuca-Gorda ridge area. *Earth Planet. Sci. Lett.* **33**, 185-207.
- Von Damm K. L., Edmond J. M., Grant B., Measures C. I., Walden B., and Weiss R. F. (1985a) Chemistry of submarine hydrothermal solutions at 21 °N, East Pacific Rise. *Geochim. Cosmochim. Acta* **49**, 2197-2220.
- Von Damm K. L., Edmond J. M., Measures C. I., and Grant B. (1985b) Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California. *Geochim. Cosmochim. Acta* **49**, 2221-2237.
- Wageman R., Brunskill G. J., and Graham B. W. (1977) Composition and reactivity of some river sediments from the Mackenzie Valley, North West Territories, Canada. *Envir. Geol.* **1**, 349-358.
- Waite T.D., Wrigley I.C., and Szymczak R. (1988) Photoassisted dissolution of a colloidal manganese oxide in the presence of fulvic acid. *Environ. Sci. Technol.* **22**, 778-785.
- Wei Ching-Ling and Murray J. W. (1991) $^{234}\text{Th}/^{238}\text{U}$ disequilibria in the Black Sea (1991) *Deep-Sea Res.* **38** (suppl.), S855-S873.

Weiss R. F. (1977) Hydrothermal manganese in the deep sea scavenging residence time and Mn/³He relationships. *Earth Planet. Sci. Lett.* **37**, 257-262.

Whitfield M., and Turner D. R. (1987) The role of particles in regulating the composition of seawater. In *Aquatic Surface Chemistry* (ed. Stumm W.), pp. 457-493. Wiley-Interscience, New York.

Wiberg K. B. (1965) In *Oxidation in Organic Chemistry* (ed. Wiberg K. B.), pp. 69-185. Academic Press, New York.

Wiberg K. B., Schafer H. J. (1969) Chromic acid oxidation of isopropyl alcohol. Preoxidation equilibria. *J. Am. Chem. Soc.* **91**, 927-932.

Wittbrodt P. R., and Palmer C. D. (1995) Reduction of Cr(VI) in the presence of excess soil fulvic acid. *Environ. Sci. Technol.* **29**, 255-263.

Wittbrodt P. R., and Palmer C. D. (1996) Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances. *Environ. Sci. Technol.* **30**, 2470-2477.

Yagi A. (1988) Dissolved organic manganese in the anoxic hypolimnion of Lake Fukami-ike. *Jpn. J. Limnol.* **49**, 149-156.

Zepp R. G., Baughman G. L., and Schlotzhauer P. F. (1981) Comparison of photochemical behaviour of various humic substances in water. I. Sunlight induced reactions of aquatic pollutants. *Chemosphere* **10**, 109-117.

Zhang H., Van den Berg C. M. G., and Wollast R. (1990) The determination of interactions of cobalt(II) with organic compounds in seawater using cathodic stripping voltammetry. *Mar. Chem.* **28**, 285-300.

APPENDIX I:**Chromium distribution in the eastern North Pacific****Table A1-1: Station P26**

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Cr(tot) (nM)
10	0.058	2.59	2.65
50	0.053	2.65	2.74
100	0.048	2.87	2.92
200	0.064	2.69	2.76
300	0.081	3.12	3.21
400	0.081	4.07	4.15
500	0.135	3.06	3.20
600	0.075	3.99	4.07
1000	0.135	3.81	3.95
1500	0.025	3.29	3.31
2000	0.067	3.80	3.87
3000	0.214	3.44	3.65
3500	0.099	3.73	3.83
4000	0.293	4.03	4.32

Table A1-2: Station P20

Depth (m)	Cr-III (nM)	Cr-VI (nM)	T Cr (nM)
20	0.156	2.21	2.36
50	0.029	2.55	2.84
100	0.079	2.55	2.63
200	0.089	2.43	2.52
300	0.072	2.89	2.96
400	0.200	3.15	3.35
500	0.135	2.71	2.85
600	0.136	2.85	2.99
800	0.098	2.61	2.71
1000	0.083	3.43	3.51
1200	0.145	3.98	4.13
1500	0.174	2.96	3.13

Chromium distribution in the central North Atlantic**Table A1-3: Station BDA**

Depth (m)	Total Cr (nM)
19	2.85
38	2.96
56	3.64
77	3.39
121	3.42
171	3.66
299	3.76
640	3.10
1468	3.17
2088	3.09
2463	3.42
3000	3.94
3500	3.33
4000	3.64

Chromium distributions in British Columbia Inlets

Table A1-4: Knight Inlet (Station KN7)

Depth (m)	Cr(III) (nM)	Cr-VI (nM)	Total Cr (nM)
10	0.77	2.65	3.42
30	0.65	2.84	3.49
50	0.69	2.86	3.55
75	0.72	3.45	4.17
100	0.75	3.46	4.21
150	0.77	3.95	4.72
200	0.35	4.38	4.73
300	0.39	3.62	4.01
400	0.61	3.74	4.35
450	0.43	4.08	4.51

Table A1-5: Dean Inlet (Station DE10)

Depth (m)	Cr-III (nM)	Cr-VI (nM)	Total Cr (nM)
10	1.43	2.78	4.21
20	1.04	3.41	4.45
30	0.36	4.13	4.49
50	0.53	3.55	4.08
75	0.39	3.83	4.22
100	0.51	3.85	4.36
120	0.56	3.24	3.85
130	0.61	3.24	3.85
150	0.65	3.22	3.87

Table A1-6: Jervis Inlet 3 (Station JV 3)

Depth (m)	Cr-III (nM)	Cr-VI (nM)	Total Cr (nM)
10	0.65	2.78	3.43
20	0.75	2.99	3.74
30	0.67	3.28	3.95
50	0.72	3.45	4.17
75	0.56	3.65	4.21
100	0.43	3.92	4.35
200	0.45	3.88	4.33
300	0.55	3.46	4.01
400	0.61	3.74	4.35
500	0.65	3.86	4.51
650	0.55	4.12	4.67

APPENDIX II: SAANICH INLET DATA (MAY 1994-JULY 1995)

Legend:

Cr(III)	Labile chromium(III)
Cr(VI)	Chromium(VI)
Tot Cr	Total labile chromium
Ox Cr	Total oxidizable chromium
D Mn	Dissolved manganese
P Mn	Particulate manganese
D Fe	Dissolved iron
P Fe	Particulate iron
P Al	Particulate aluminum
ND	Not Determined

MAY 1994

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.56	3.05	3.61			6.8	0.03	89	28.5	58.0
30	0.54	2.65	3.19			9.3	0.56	94	55.0	149
50	0.77	2.39	3.16			9.9	0.55	23	31.0	70.7
70	0.64	2.77	3.41			14	0.10	32	30.5	67.9
90	0.81	2.03	2.84			15	3.10	48	139	427
120	0.48	1.05	1.53			340	41.0	95	92.6	305
140	0.71	0.15	0.86			1410	1.09	270	116	173
160	0.51	0.34	0.85			1440	1.62	380	247	136
180	0.43	0.38	0.81			1470	1.74	290	243	1144
200	0.55	0.25	0.80			1520	2.14	340	310	88.6

JUNE 1994

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.48	2.66	3.14		355	12	3.78	110	56.7	124
30	0.46	2.58	3.04		220	13	3.83	140	65.8	144
50	0.63	2.49	3.12		ND	18	3.65	140	69.6	168
70	0.77	2.51	3.28		138	46	2.55	160	74.6	261
90	0.59	2.70	3.29		ND	62	16.3	90	313	983
100	0.63	2.64	3.27		ND	72	9.68	24	269	322
110	0.47	2.78	3.25		81.3	44	1.03	35	93.6	302
120	0.80	2.05	2.85		56.7	64	35.3	27	228	253
130	0.22	1.03	1.25		8.04	180	70.2	45	80.0	274
140	0.40	0.29	0.68		2.23	1990	0.61	36	77.0	98.7
150	0.25	0.68	0.92		0.45	ND	ND	ND	ND	ND
160	0.30	0.45	0.74	1.63	0.00	1980	2.04	310	371	117
180	0.53	0.46	0.99		0.00	1950	2.33	350	315	120
190	0.46	0.36	0.82		0.00	1030	0.96	460	201	202
200	ND	ND	ND		ND	68	3.76	410	100	211

JULY 1994

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (µM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.37	2.38	2.75		226	8.4	1.28	170	60.1	137
30	0.37	3.09	3.46		191	13	1.53	71	52.0	119
50	0.51	2.26	2.77	2.85	154	8.2	1.56	ND	37.0	149
70	0.61	1.89	2.50		73.7	7.5	6.56	110	119.8	331
100	0.25	2.04	2.28		23.2	9.3	16.9	12	160.5	379
110	0.33	1.55	1.88		29.9	38	44.4	ND	88.2	1050
120	0.39	1.33	1.72		19.7	90	84.3	ND	197.0	619
130	0.46	0.57	1.02		3.10	660	47.30	48	199.0	699
140	0.50	0.17	0.67	1.29	2.20	1040	2.04	230	193.9	219
160	0.38	0.32	0.71	1.61	0.00	1160	1.48	330	369.9	96.0
180	0.60	0.19	0.79	1.82	0.00	1200	1.47	500	482.0	105
200	0.66	0.09	0.75	1.93	0.00	1210	1.50	440	465.3	88.0

AUGUST 1994

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (µM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.64	2.64	3.28		296	8.6	0.24	130	12.7	688
30	0.48	2.78	3.26		139	7.4	0.72	120	88.4	532
50	0.83	2.98	3.81		124	7.5	0.82	150	50.0	152
70	0.53	2.71	3.24		45.6	30	11.0	110	133.3	1360
100	0.38	2.52	3.00		29.9	42	32.3	120	122.9	578
110	0.50	2.34	2.84		34.4	86	40.9	120	106.8	419
120	0.58	2.26	2.84		25.9	160	61.2	180	79.8	566
130	0.46	1.48	1.94		21.4	410	41.2	250	82.9	459
140	0.64	0.94	1.58		8.50	800	39.7	310	87.5	414
160	0.63	0.32	0.94		0.50	1420	0.96	600	216.1	272
180	0.54	0.81	1.35		0.00	1000	0.32	190	264.9	1390
200	0.47	0.89	1.36		0.00	1090	0.66	1000	315.9	139

SEPTEMBER 1994

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μ M)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.44	3.57	4.01		410	16	0.29	160	12.5	546
30	0.61	3.31	3.92		151	15	0.21	230	15.4	568
50	0.64	3.73	4.37		128	16	0.44	220	27.3	235
70	0.58	3.28	3.86		38.4	15	4.83	150	77.7	1568
100	0.36	2.38	2.74		5.80	740	37.6	560	41.2	657
110	0.62	1.78	2.40		9.40	570	51.7	270	44.8	344
120	0.81	1.89	2.70		9.80	380	49.9	280	224.1	299
130	0.76	0.78	1.54		2.70	1240	36.8	700	125.6	97.9
140	0.59	0.92	1.51		0.00	1020	42.5	710	72.6	76.6
160	0.62	2.31	2.94		13.0	490	56.7	470	44.1	235
180	0.85	2.28	3.13		25.0	420	63.6	220	56.7	255
200	0.81	2.04	2.85		27.2	310	73.7	150	65.7	306

OCTOBER 1994

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μ M)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.52	4.59	5.14		138	14	2.47	120	38.5	89.0
30	0.37	4.32	4.69		142	17	3.66	150	66.3	306
50	0.58	4.86	5.44		87.5	23	7.05	120	456	372
70	0.67	4.37	5.04		137.1	29	4.96	150	291	1410
100	0.5	1.87	2.36		11.6	1130	19.5	140	214	533
110	0.47	1.65	2.11		8.04	950	68.7	150	149	235
120	0.49	1.45	1.94		7.15	1300	30.4	140	155	221
130	0.45	2.21	2.66		4.91	85	66.7	180	53.3	68.1
140	0.38	2.83	3.21		11.61	35	97.7	180	84.1	212
160	0.41	2.58	2.99		22.78	31	90.5	200	64.9	199
180	0.51	2.5	3.05		29.47	31	93.0	290	62.3	200
200	0.49	2.35	2.84		22.78	870	114	40	39.4	138

NOVEMBER 1994

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.465	2.756	3.22		ND	14	0.72	100	31.80	151
30	0.558	2.253	2.81		172	17	1.89	140	103.7	334
50	0.515	2.995	3.51		205	23	1.81	130	312.1	1335
70	0.485	2.575	3.06		198	29	2.79	150	769	4754
100	0.472	2.000	2.47		122	1140	14.4	150	2276	5150
110	0.482	1.378	1.86		5.81	950	48.4	130	231.5	631
120	0.476	1.321	1.80		2.68	1300	69.7	130	67.8	389
130	0.490	1.395	1.89		2.23	85	52.9	130	48.5	189
140	0.456	2.016	2.47		5.36	35	53.4	140	46.1	136
160	0.476	2.357	2.83		5.81	31	69.5	160	45.8	226
180	0.510	2.816	3.33		5.36	31	148	160	48.0	158
200	0.503	2.917	3.42		3.13	870	115	200	20.0	79.6

JANUARY 1995

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.799	3.630	4.43		249	11	0.50	79	56.87	145
30	0.884	3.976	4.86		236	14	0.49	88	44.87	333
50	0.598	4.072	4.67	4.56	228	11	0.54	98	41.67	240
70	0.480	4.800	5.28		212	23	0.76	100	38.43	9909
100	0.643	3.410	4.06		76.8	23	0.82	120	37.19	2601
110	0.844	2.130	3.26		12.1	15	14.8	180	120.5	1324
120	0.794	2.490	3.28		4.47	150	15.3	240	34.65	346
130	0.805	2.640	3.44		5.36	270	6.64	140	7.35	234
140	0.554	2.540	3.10		6.70	240	10.9	180	9.62	176
160	0.385	3.040	3.43	3.48	6.70	680	8.80	270	3.14	187
180	0.676	2.604	3.28		8.93	890	6.78	270	3.060	146
200	0.742	2.663	3.41	3.51	8.04	1070	4.57	300	2.46	177

FEBRUARY 1995

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	1.37	2.58	3.95		ND	13	1.02	76	284.4	856
30	1.11	3.03	4.14		237	12	0.43	35	91.1	155
50	1.18	3.17	4.35		ND	13	0.53	25	61.8	165
70	1.26	3.22	4.48		222	11	1.19	26	234	831
100	1.22	2.26	3.48		37.5	24	7.11	26	261.0	1276
110	1.13	2.4	3.53		ND	30	12.1	99	203.0	758
120	ND	ND	ND	ND	21.0	50	2.58	89	171.0	1007
130	1.02	1.87	2.89		2.70	220	9.34	100	38.7	144
140	0.92	1.63	2.58	2.65	4.50	290	7.52	120	36.9	98.7
160	0.78	1.73	2.51		4.50	810	11.3	140	55.5	145
180	0.89	1.33	2.22	2.45	2.20	1080	9.09	190	78.5	140
200	0.83	1.28	2.11	2.23	4.00	1570	1.05	310	85.8	181

MARCH 1995

Depth (m)	Cr(III) (nM)	Cr(III) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	1.90	4.09	6.00		299	12	0.99	200	92.2	429
30	1.68	3.96	5.64		256	15	1.04	195	69.7	306
50	2.56	4.07	6.62		241	14	1.14	177	56.9	225
70	1.89	4.76	6.65		243	4.8	1.08	208	54.6	242
100	1.48	3.08	4.56		72.8	10	3.35	245	155.6	729
110	1.06	2.98	4.04		29.0	12	9.82	286	165.1	690
120	1.15	1.92	2.67		12.5	38	13.61	299	84.1	328
130	1.06	2.08	3.14		6.70	230	8.62	317	63.6	152
140	0.92	1.65	2.57		6.70	310	5.59	291	49.4	173
160	1.02	1.10	2.12		6.30	810	3.84	213	16.9	20.6
180	1.67	0.29	1.96		6.70	1100	5.42	336	33.4	46.9
200	1.93	0.19	2.12		4.50	1440	3.87	765	60.6	55.6

APRIL 1995

Depth (m)	Cr(III) (nM)	Cr(III) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.733	4.590	5.320		331	36	0.17	194	2.570	16.2
30	0.628	---	ND		260	36	0.88	204	25.58	90.5
50	1.100	4.140	5.240		253	18	0.80	196	24.02	86.6
70	0.770	4.510	5.280		230	36	1.40	206	34.78	149
100	1.230	4.180	5.410		66.1	37	2.57	210	91.01	337
110	1.160	3.000	4.160		13.4	39	5.00	332	36.09	177
120	1.340	2.250	3.590		5.81	130	14.7	261	38.84	116
130	0.806	2.830	3.640		4.47	530	7.03	251	35.39	84.2
140	0.990	1.540	2.530		7.60	640	5.28	264	29.59	76.8
160	1.050	2.010	3.060		4.91	1180	8.56	271	30.96	59.5
180	1.480	2.460	3.940		24.6	940	5.28	737	23.92	57.5
200	1.340	0.940	2.280		4.47	1680	25.0	840	79.23	52.2

MAY 1995

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μM)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	1.250	5.940	7.190		318	14	1.26	249	40.70	144
30	1.470	5.224	6.690		282	12	1.75	231	79.60	249
50	2.410	4.130	6.550		247	16	0.63	223	19.57	74.3
70	2.320	4.870	7.190		183	17	0.16	214	6.56	31.4
100	1.620	3.860	5.480		54.9	15	1.45	265	50.43	173
110	1.290	3.540	4.830		21.4	26	1.64	240	35.81	147
120	1.180	2.940	3.220		8.49	87	3.85	334	27.44	121
130	2.050	1.160	3.220		6.25	200	1.35	279	6.37	17.3
140	2.540	1.370	3.910		6.25	480	3.77	223	13.50	30.6
160	1.300	2.390	3.690		6.25	970	ND	284	ND	ND
180	1.720	1.170	2.890		4.02	1320	9.23	340	34.10	113
200	1.050	ND	ND		4.02	1500	6.51	366	26.07	51.1

JULY 1995

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Tot Cr (nM)	Ox Cr (nM)	O ₂ (μ M)	D Mn (nM)	P Mn (nM)	D Fe (nM)	P Fe (nM)	P Al (nM)
10	0.45	3.22	3.65		282	12	0.92	122	7.240	23.0
30	0.42	3.55	3.97		167	14	0.85	3110	25.66	47.7
50	0.52	3.08	3.60		137	13	1.31	212	26.97	47.4
70	0.48	2.58	3.06		66.5	12	5.93	216	103.3	388
100	0.46	2.29	2.75		49.6	21	19.0	456	250.5	847
110	0.37	1.84	2.21		51.4	25	36.0	391	607.2	2347
120	0.56	1.29	1.85		41.1	40	32.3	368	160.0	827
130	0.55	1.10	1.65		31.7	46	29.0	275	211.4	662
140	0.54	0.69	1.23		7.60	330	41.5	164	84.38	263
160	0.64	0.35	0.99		0.00	1350	3.83	343	73.75	92.0
180	0.66	0.23	0.89		0.00	1410	0.84	464	99.36	54.0
200	0.65	0.13	0.78		0.00	1530	0.30	820	103.1	41.4

APPENDIX III: Chromium distribution in the Black Sea and the Juan de Fuca Ridge

Table AIII-1: Station BS3-6 in the Black Sea

Depth (m)	Total Cr (nM)
30	2.60
45	2.33
55	2.22
75	1.61
80	1.58
85	1.74
90	1.75
95	1.98
100	1.84
105	2.00
110	2.28
115	2.15
120	2.19
130	2.43
140	2.48
170	2.65
200	2.61
250	2.90

Table AIII-2: Station JDFR-1 in the Juan de Fuca Ridge

Depth (m)	Cr(III) (nM)	Cr(VI) (nM)	Total Cr (nM)
100	0.91	3.38	4.29
200	0.66	4.08	4.74
400	0.86	3.77	4.63
700	0.98	3.67	4.65
1400	1.05	2.97	4.02
1550	1.04	3.51	4.55
1725	1.24	5.04	6.28
1810	1.37	5.05	6.42
1860	1.35	4.73	6.08
1910	1.41	4.80	6.21
1975	1.86	4.10	5.96
2075	1.68	4.34	6.02
2225	1.70	4.50	6.20