

**SOURCES OF Mn, Al, Cd AND Cu TO COASTAL WATERS OF THE  
CALIFORNIA CURRENT SYSTEM**

**By**

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**We accept this thesis as conforming to the required standard**

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### Abstract

Dissolved Mn, Al, Cd and Cu concentrations were determined across a series of horizontal surface transects along the Northeast Pacific Ocean from the coast off Big Sur, California to Vancouver Island, British Columbia. This region of coastline allows the relative importance of different modes of input of trace metals to California Current surface waters to be assessed. In particular, the impact on dissolved concentrations of fluvial input from the Columbia River, diffusion from reducing shelf sediments and/or sediment resuspension coupled with upwelling, and the width of the continental shelf were examined. In addition, Mn, Al, Cd and Cu distributions were compared with Fe and Ga data from the same region.

Background California Current surface water values were determined for Mn (3-5nmol/kg), Al (0.38-0.65nmol/kg), Cd (0.08-0.30nmol/kg) and Cu (0.79-1.51nmol/kg). These data agree well with previous work.

According to this study, the Columbia River is a considerable source of Mn and Al to California Current surface waters, with the highest levels of Mn and Al for all transects observed coincident with the lowest salinity waters sampled (Mn up to 117nmol/kg; Al up to 1.1nmol/kg). Metal versus salinity plots for both Mn and Al indicate non-conservative mixing and removal as the water ages. Al is removed significantly faster than Mn and Ga. This agrees well with previous estimates of surface ocean residence times for these elements. In contrast to Mn and Al, Cd does not show enrichment in low salinity waters. However, it is possible that the Columbia may well be providing small quantities of Cd to California Current waters, but in this area the input is masked by relatively higher background signals. No data for Cu were available for the Columbia River area.

Summer upwelling off the coasts of Oregon, Washington and California supplied significant quantities of Mn (4.6-39.5nmol/kg), Cd (0.32-0.92nmol/kg) and Cu (1.66-4.52nmol/kg) to California Current surface waters. For Mn and Cu, diagenic remobilization and/or sediment resuspension coupled with upwelling explains the elevated signals for these metals. For Cd, the elevation is attributable to transport of enriched bottom water to the surface by upwelling. For Al, either sediments in this area are not a significant source of this metal, or Al is indeed supplied by sediments but is then stripped out of the water at a dramatic rate.

Mn and Cu (as well as Cd and Al to a lesser extent) showed high elevation coincident with transects overlying areas where the continental shelf is wide, and significantly lower elevation coincident with transects overlying areas where the continental shelf is narrow. This again emphasizes the potential impact of sediments on trace metals concentrations in surface waters.

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## Glossary

|        |   |
|--------|---|
| AcOH   | Acetic acid                                       |
| CC     | California Current                                |
| CCS    | California Current System                         |
| Chl a  | Chlorophyll a                                     |
| cm     | centimeter  |
| CUC    | California Undercurrent                           |
| CTD    | conductivity-temperature depth                    |
| DC     | Davison Current                                   |
| DDW    | distilled deionized water                         |
| FEP    | fluorinated ethylene propylene                    |
| GFAAS  | graphite furnace atomic absorption spectrometry   |
| HEPA   | high efficiency particle air                      |
| HDPE   | high density polyethylene                         |
| HNCL   | high nitrate low chlorophyll                      |
| HOAc   | acetic acid                                       |
| hrs    | hours   |
| ICP/MS | inductively coupled mass plasma mass spectrometry |
| kg     | kilogram  |
| km     | kilometer   |
| L      | liter   |
| m      | meter   |
| M      | molarity  |
| mg     | milligram   |
| min    | minute  |
| mL     | milliliter  |
| mm     | millimeter  |
| N      | normality   |
| ng     | nanogram  |
| nM     | nanomolar   |

|                 |   |
|-----------------|---|
| NOAA            | National Oceanic and Atmospheric Administration |
| pm              | picometer                                       |
| pM              | picomolar                                       |
| ppb             | parts per billion                               |
| PTFE            | poly(tetrafluoroethylene)                       |
| REE's           | rare earth elements                             |
| RSD             | relative standard deviation                     |
| s               | second  |
| S               | salinity <sup>1</sup>                           |
| T               | temperature                                     |
| $\tau$          | residence time                                  |
| $\mu\text{L}$   | microliter                                      |
| $\mu\text{mol}$ | micromole                                       |
| yr              | year  |

<sup>1</sup> According to the Practical Salinity Scale, salinity is dimensionless.

## **Chapter 1: Introduction**

### **1.1 Trace Metal Geochemistry in the Marine Environment**

#### **1.1.1 Background**

Over the past two decades, our understanding of trace metal biogeochemistry in marine systems has increased significantly, and most of the elements in the periodic table have now been detected in seawater at levels ranging from femtomolar to millimolar. Those metals present at concentrations less than a few parts per billion (ppb) are termed trace metals and interest in their environmental impact has sparked intense research into their chemical, biological and geological behavior in riverine, lake and ocean environments.

Recent technology advances, eliminating decades old problems of contamination and insufficient sensitivity, allow even those elements present at concentrations as low as femtomolar to be detected from a seawater matrix quickly and accurately. The initial critical breakthroughs arrived in the mid to late 1970's with clean sampling techniques developed by Boyle and co-workers (1977) for Cu, Cd and Ni; Bruland and co-workers (1979) for Cu, Cd, Zn and Ni; and Schaule and co-workers (1981) for Pb becoming the accepted standard for trace metal analysis. Simultaneous advances in the development of sensitive analytical techniques sparked interest in the use of graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and differential pulse anodic stripping voltammetry (DPASV). Today, elimination and/or control of contamination, and widespread availability and use of instruments capable of extremely low detection limits allows oceanographically consistent data-sets for many trace metals to be obtained.

#### **1.1.2 Trace metal distributions in seawater**

The distribution and concentration of trace metals in the ocean are determined by their relative rates of supply and removal. Trace metals are supplied to the ocean from riverine, hydrothermal, atmospheric and anthropogenic inputs and via sediment diagenesis. Removal pathways include scavenging (adsorption to sinking particles),

precipitation due to changes in redox conditions, biological uptake and hydrothermal vent circulation. These interactions determine the amount of time a trace metal resides in the ocean before it is removed, and we can estimate this 'residence time' by assuming that the ocean is a uniformly mixed reservoir at steady state. However, it is important to realize that this assumption regarding the ocean existing as a uniformly mixed reservoir does not hold completely true, and that trace metal distributions can vary widely. These variations will be discussed in the next section. Steady state simply refers to the idea that rates of supply of the constituent of interest are equal to rates of removal. The residence time may thus be defined as:

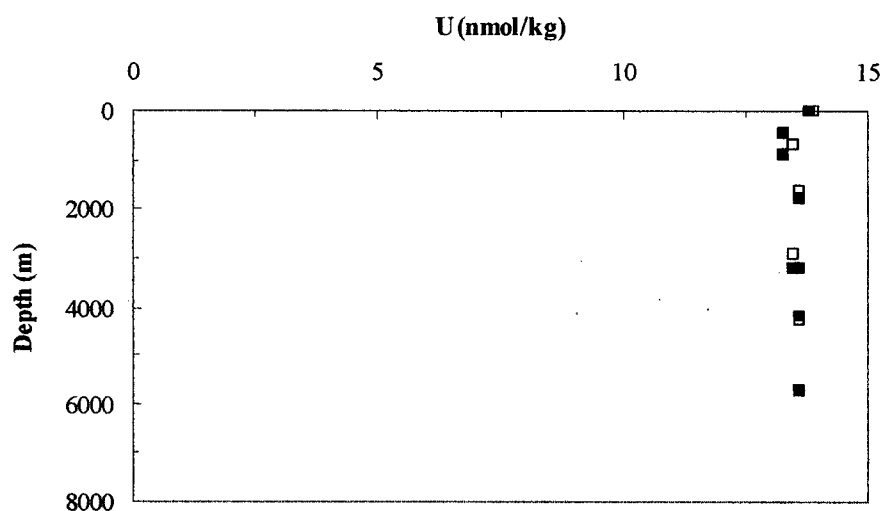
$$\tau = \text{Total amount of trace metal dissolved in ocean} / \text{rate of supply or removal}$$

(steady state conditions are assumed)

Three major distribution profiles are observed: conservative, nutrient and reactive.

#### 1.1.2.1 Conservative Distribution

Conservative trace metals exhibit constant concentration relative to salinity. These metals have low reactivity and are influenced solely by physical processes such as advection, and turbulent mixing. Residence times are long, typically between  $10^5$ - $10^7$ yr, and concentrations are high relative to crustal abundance. Examples of conservative metals include sodium, uranium, molybdenum and tungsten. Uranium's distribution is shown in figure 1.1.2.1.1.



**Figure 1.1.2.1.1**

**U versus depth in the Atlantic and Pacific Oceans.**

**(Legend: ■=Pacific data; □=Atlantic data)**

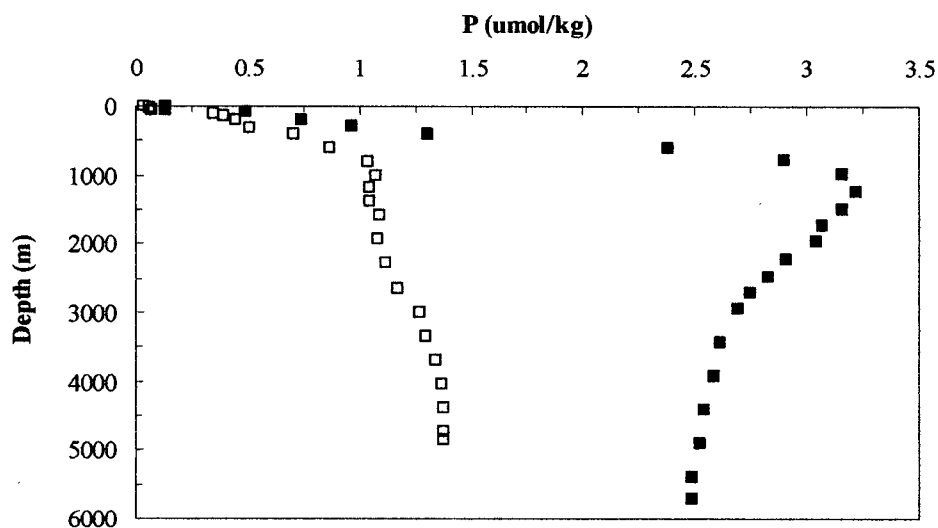
(Ref. Chen *et al*, 1986)

Dissolved uranium has a conservative distribution in the ocean. Concentrations are relatively uniform vertically and horizontally and change only in proportion to salinity.

#### 1.1.2.2 Nutrient Distribution

Nutrient type metals exhibit surface depletion and deep water enrichment in an analogous manner to the major nutrients, nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{HPO}_4^{2-}$ ) and silicic acid ( $\text{H}_4\text{SiO}_4$ ). The metal is removed from surface waters by biological uptake and is subsequently regenerated at depth as the biological matter sinks and is then oxidized or resolubilized. Metals (such as Cd) associated with the more labile nutrients,  $\text{NO}_3^-$  and  $\text{HPO}_4^{2-}$ , typically show maximum concentrations around 1000m. Those associated with  $\text{H}_4\text{SiO}_4$  (such as Zn) show maxima at or below 2500m. Inter-ocean fractionation is observed for all nutrient type metals, with Pacific deep water concentrations at least three times higher than those of the deep Atlantic. Residence times are intermediate, typically

between  $10^3$  to  $10^5$ yr. A typical nutrient distribution (that of P) is shown in figure 1.1.2.2.1 and a typical nutrient-type metal distribution (that of Zn) is shown in figure 1.1.2.2.2.

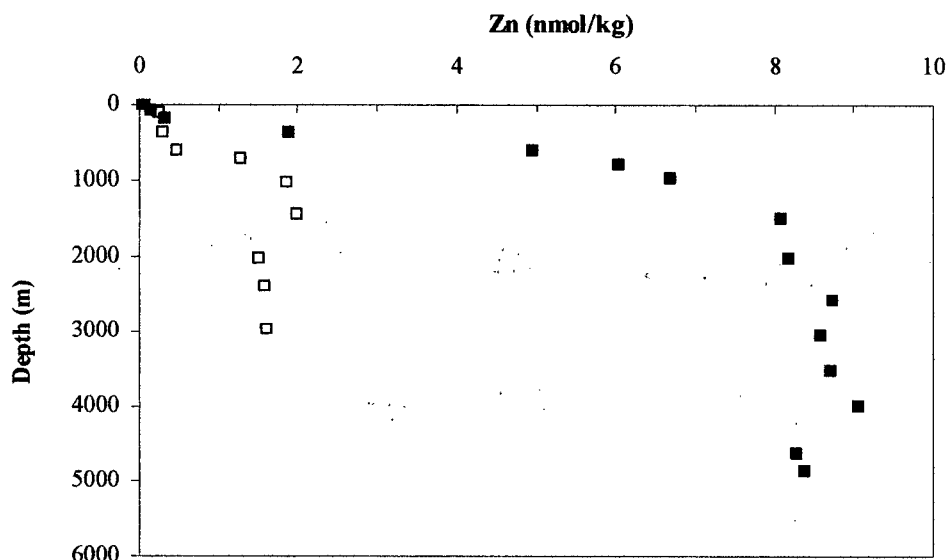


**Figure 1.1.2.2.1**

**Phosphorous profiles from the Pacific and Atlantic Oceans.**

**(Legend: ■=Pacific data; □=Atlantic data)**

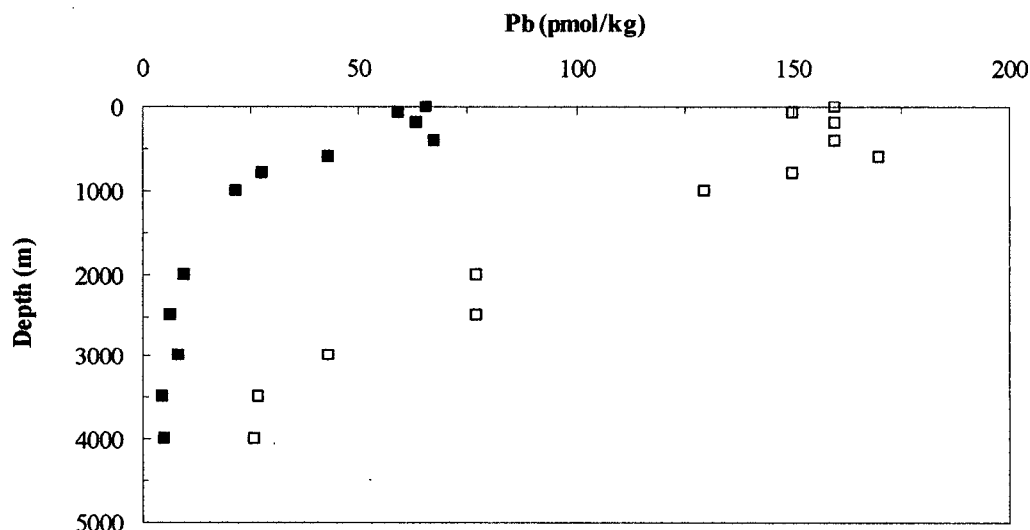
(eWOCE Atlas: Pacific cruise 18DD9403/1, Station WO43W; Atlantic cruise 320C202/1, Station 50; Moss Landing Laboratories)



**Figure 1.1.2.2.2**  
**Zinc profiles from the Atlantic and Pacific Oceans.**  
 (Legend: ■=Pacific data; □=Atlantic data)  
 (Bruland, 1980; Bruland and Franks, 1983)

### 1.1.2.3 Reactive distribution

Reactive or scavenged trace metals generally exhibit surface enrichment due to atmospheric deposition and/or riverine input, deep water enrichment due to sediment input, and removal with distance from the source via intense and rapid adsorption onto sinking particles. This rapid removal results in strong source imprints for these metals (for example Al and Pb). Thus reactive trace metals may be used as highly effective tracers of transport and mixing mechanisms in the ocean. Residence times are short, on the order of  $<10^3$  yr, and concentrations are low relative to crustal abundance. The distribution of Pb is shown in figure 1.1.2.3.1. For many reactive trace metals (for example Mn), variations on the typical profile described above are observed reflecting the complexity of the biogeochemical controls of these metals.



**Figure 1.1.2.3.1**

**Lead profiles from the Pacific and Atlantic Oceans.**

**(Legend: ■=Pacific data; □=Atlantic data)**

(Schaule and Patterson, 1981; 1983)

## **1.2 Marine geochemistry of aluminium, manganese, cadmium and copper**

### **1.2.1 Aluminium**

#### **1.2.1.1 Introduction**

Aluminium (Al), the most abundant metallic element in the Earth's crust (8.23% by weight), is a mono-isotopic, trivalent metal with a strong tendency to hydrolyze in seawater to form the particle reactive species  $\text{Al}(\text{OH})_3$  and  $\text{Al}(\text{OH})_4^-$  (Orians and Bruland, 1986). These species are both important in seawater, and a switch in speciation from mostly  $\text{Al}(\text{OH})_4^-$  (75%) in surface waters to  $\text{Al}(\text{OH})_3$  in deeper waters is observed. Dissolved Al has a large dynamic range in the oceans with concentrations ranging from  $<0.06\text{nmol/kg}$  in mid-depth North Pacific waters (Orians and Bruland, 1988) to  $650\text{nmol/kg}$  in the surface micro layer of the Arabian Sea (Narvekar and Singbal, 1993). In the open ocean, Al displays an inter-ocean fractionation opposite to that of the nutrients, with values in the Pacific 8 to 40 times lower than those at similar depths in the Atlantic (Orians and Bruland, 1985, 1986).

Al is a non-essential element and exhibits a scavenged distribution. Typically,



vertical profiles for Al exhibit a surface maximum, a mid-depth minimum, and increasing concentrations with depth below 1000m. However, in certain regions the behavior is somewhat anomalous and there is either no surface maximum or only a slight increase in concentration between intermediate and bottom waters. The disparity in Al distributions in different oceanic regions has led to a degree of controversy regarding both the sources and removal mechanisms responsible for the distribution of Al. Deep ocean residence times, estimated using vertical advection diffusion scavenging models, vary from 30-200yr depending on the flux of particles from overlying waters (Orlans and Bruland, 1985). The residence time of Al in surface waters is estimated to be on the order of 3 to 4yr in the oligotrophic waters of the central North Pacific gyre (Orlans and Bruland, 1986). The low background of Al in the oceans, and the large crustal concentration combine to make Al an excellent tracer of dust deposition to the oceans and of advective movement of water masses (Measures and Edmond, 1990).

#### 1.2.1.2 Source and Removal Pathways

Surface water dissolved Al concentrations range from 0.3-5nmol/kg in the Pacific Ocean (Orlans and Bruland, 1986, 1988) to 0.5-85nmol/kg in the Atlantic and Mediterranean (Measures, 1995; Measures *et al* 1984, 1986; Morley *et al*, 1992; van den Berg, 1994) and 10-300nmol/kg in the Arabian Sea (Narvekar and Singbal, 1993). The surface distribution is tightly correlated with the magnitude of dust input to surface waters, and partial dissolution (5-10%) of atmospherically transported continental dust has been proposed as the dominant mode of input of Al to surface waters of the open ocean (see for example Hydes, 1983; Measures *et al*, 1984; Orlans and Bruland, 1986; Maring and Duce, 1987; Chester *et al*, 1991; van den Berg *et al*, 1994). Evidence for this includes decreasing concentrations with decreasing salinity seen in the coastal surface waters of the western North Atlantic (Measures *et al*, 1994), and eastern North Pacific (Orlans and Bruland, 1986), and the surface maximum observed in many areas of the world's oceans. For example, work by Chester *et al* (1985, 1991) points to significant dust impact in the Arabian Sea region, with atmospheric Al concentrations over the northern Arabian Sea among the highest recorded for the marine environment. Recent work by Narvekar and Singbal (1992) in the same region recorded high open surface

water Al concentrations (37-52nM and 11-300nM, respectively). Fluvial input, while locally significant is rapidly attenuated through removal in shelf and slope waters in highly productive coastal regions (Hydes and Liss, 1977; van Bennekom *et al*, 1978; Measures *et al*, 1984; Morris *et al*, 1986). However, in some regions such as the North Sea (Kremling and Hydes, \ 1988), coastal waters of the Arabian Sea (Narvekar and Singbal, 1993) and the Panama Basin (Measures *et al*, 1984) fluvial input is thought to be a significant source of dissolved Al.

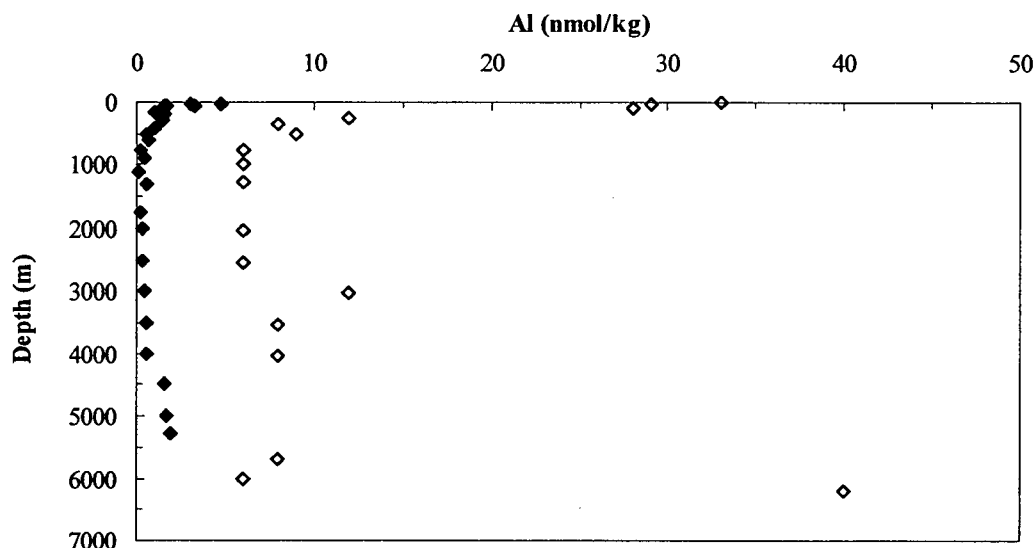
Deep water dissolved Al concentrations range from 0.5-2.0nmol/kg in the Pacific to 8-30nmol/kg in the Atlantic to 135-170nmol/kg in the Mediterranean. This inter-ocean fractionation, the largest observed for any element, is explained by the continual removal of Al as deep waters travel from their source region in the western North Atlantic to the eastern North Atlantic and on to the North Pacific. Elevated levels of dissolved Al are observed in the deep relative to the intermediate waters of the Pacific (Yeats and Brewers, 1985), the western North Atlantic (Jickells and Burton, 1988), and the Arctic (Yeats *et al*, 1992). Seemingly, this increase in concentration observed between the mid-depth minimum and the sediment water interface indicates the presence of a deep water source of Al. Diffusion out of sediments, desorption of Al from particle surfaces, release during the dissolution of a biogenic carrier and a pressure dependent equilibrium of dissolved Al with some solid phase such as a pelagic red clay have all been suggested as potential deep waters sources (Orians and Bruland, 1985). However, the inverse relationship between deep water age and deep water Al concentrations, and the fact that deep water Pacific concentrations are only very slightly elevated above those of intermediate waters, argue against diffusion from sediments or a pressure dependent equilibrium as being significant sources of Al to deep waters. And authors such as Measures *et al* (1986, 1995) suggested an alternate source of Al proposing the high Al concentrations observed in the deep waters of the Western and Eastern North Atlantic to be due to advection of northern European shelf waters enriched in dissolved Al from river runoff.

The mechanism by which Al is removed from the water column has been a subject of some controversy. Early evidence suggested that biological uptake impacted Al removal to a significant degree. Apparent Al-Si correlations observed in the surface

waters of the Mediterranean (see for example Cassetto and Wollast, 1979) and the Norwegian, Greenland and Iceland Seas (van Beusekom, 1988) were interpreted as resulting from Al being actively removed by phytoplankton and regenerated at depth along with silicate. Laboratory evidence also suggested active uptake of Al into biological soft tissues and/or silica frustules as well (see for example Stoffyn, 1979; Moran and Moore, 1988). In contrast, Orians and Bruland (1985, 1986) argued that the removal of Al occurs primarily via scavenging; a passive adsorption onto the surface of particles. Particle types responsible for the scavenging of dissolved Al may be inorganics (such as biogenic opal, clay minerals, or iron and manganese oxyhydroxides), organics, and inorganic substrates with an organic coating. It seems that the markedly different distributions of dissolved Al and silicate in the open ocean, together with their opposite inter-ocean fractionation support a passive adsorption mechanism as opposed to biological. And it is now widely accepted that while there may be a degree of biological removal in surface open-ocean waters, intensive scavenging in deeper waters predominates.

#### 1.2.1.3 Profiles

Vertical profiles of Al have been obtained for the Eastern Atlantic (Measures, 1995; Hydes, 1983), the Northwest Atlantic (Measures *et al*, 1984,1986), near the Mid Atlantic ridge (Hydes *et al*, 1986; Lunel *et al*, 1990), the high latitude North Atlantic (Olafsson, 1983), the Arctic (Moore, 1981), the Mediterranean Sea (Stoffyn and Mackenzie, 1982; Cassetto and Wollast 1979; van den Berg *et al*, 1994 ), the Eastern Arabian Sea (Narvekar and Singbal, 1993), the Indian Ocean (Measures and Vink, 1999), the Scotia and Weddell Seas (van Bennekom *et al*, 1991), and the North Pacific Ocean (Orians and Bruland, 1985, 1986). Representative profiles for the Atlantic and Pacific Oceans are shown in figure 1.2.2.3.1



**Figure 1.2.1.3.1**  
**Al versus depth in the Atlantic and Pacific Oceans**  
**(Legend: ◆=Pacific data; ◇=Atlantic data)**  
 (Orians and Bruland, 1986; Hydes, 1983)

Early investigations of the distribution of dissolved Al focused on the Mediterranean Sea. Mackenzie *et al* (1978) and Cassetto and Wollast (1979) observed relatively high concentrations of Al (about 30-170nM) in the water column and a nutrient-like vertical profile. These authors also reported a good correlation between dissolved Al and Si and concluded that biological processes were the principle controls of the vertical distribution of this element. Later studies confirmed the anomalous characteristics of dissolved Al in the Mediterranean Sea: high concentrations and nutrient like distributions (for example van den Berg *et al*, 1994).

Subsequent to the initial Mediterranean investigations, several authors began focusing on the Atlantic. For example, Hydes (1979) presented data from the northwest Atlantic at  $\sim 41^{\circ}\text{N}$  showing Al concentrations five times lower than those of the Mediterranean and no correlation with silica. The profiles exhibited a surface maximum (38nM), a pronounced minimum (20nM) at 1200m and increasing concentration with depth to bottom water values similar to those of the mixed layer. Moore and Millward

(1984) subsequently presented data from the Mid Atlantic ridge showing lower surface (13-16nmol/kg) and similar deep water signals compared to the data from Hydes. Measures *et al* (1984) reported high surface concentrations (30-65nM) of Al in waters of the northwest Atlantic and Caribbean. These authors observed significant depletion of Al (8-15nM) in low salinity shelf and slope coastal waters of the Western Atlantic. They also presented a vertical profile from the Panama Basin that was similar to those recorded in the northeast Atlantic (see below) but with significantly lower concentrations in deep and bottom waters (1-6nM).

Hydes (1983) extended his early work to the northeast Atlantic (from 25°N to 34°N), reporting similar high surface values (up to 32nM) to those in the west with concentrations increasing toward the maximum of the Saharan dust plume; interestingly a deep water increase was not observed, instead values were low ( $\leq 10$ nM) and uniform. Olafsson (1983) reporting from ~60°N in the far Northeast Atlantic just south of Iceland, observed significantly lower surface water values (~8nmol/kg) compared with Hydes, but very similar deep water signals (up to 23nmol/kg).

Measures (1995) and Hall and Measures (1998) analyzed samples from the southern, western and eastern basins of the central Atlantic and interpreted the distribution of Al in terms of advective movement of the various water masses that appear within the stations.

Orians and Bruland (1985, 1986, 1988) have presented the bulk of the data on the Al distributions in the Pacific Ocean. They reported data showing similar vertical distribution features to that seen for Al in the central North Atlantic but with concentrations in the central north Pacific being 8-40 times lower than those at corresponding depths in the central North Atlantic. Concentrations ranged from 0.3-5nM in surface waters, from 0.1-1nM in mid depths and from 0.5-2nM in deep waters. Dissolved Al concentrations were lowest in the eutrophic, low salinity California Current (0.3-1nM) and increased into the subtropical gyre of the North Pacific (5nM).

Several authors have presented work from the Arabian Sea. For example, Narvekar and Singbal (1992) reported extremely high concentrations in the surface microlayer during the summer and winter monsoon periods (23-657nM). The characteristic Al decrease in deeper waters indicated intense scavenging throughout the

water column, and a residence time of 8.4yr for Al in the Arabian Sea, with respect to the combined input of Al from fluvial and atmospheric sources, was proposed.

In summary, Al is a non-essential element and exhibits a scavenged distribution. Generally, vertical profiles of dissolved Al exhibit a surface maximum, a mid-depth minimum and increasing concentrations toward the sediment-water interface. The primary input of Al to the ocean is via the partial dissolution of eolian material. Fluvial input may be locally significant, but is typically rapidly removed through irreversible scavenging and this scavenging prevents the fluvial input from extending beyond coastal waters. Several authors have suggested a deep water source of Al involving diffusion out of sediments, desorption of Al from particle surfaces, release during the dissolution of a biogenic carrier and/or a pressure dependent equilibrium of dissolved Al with some solid phase. However, other authors have argued against a deep water source. Removal of dissolved Al predominantly involves intensive scavenging in deeper waters.

The average dissolved Al concentration in the oceans is  $\sim 1.1 \text{ nmol/kg}$  (Orlans and Merrin, 2001) with concentrations ranging from  $< 0.06 \text{ nmol/kg}$  in mid-depth North Pacific waters to  $650 \text{ nmol/kg}$  in the surface micro layer of the Arabian Sea. Pacific values are 1-2 orders of magnitude lower than in the Atlantic. Deep ocean residence times vary from 30-200yr depending on the flux of particles from overlying water; while surface water residence times are estimated to be on the order of 3 to 4yr in the oligotrophic waters of the central North Pacific gyre.

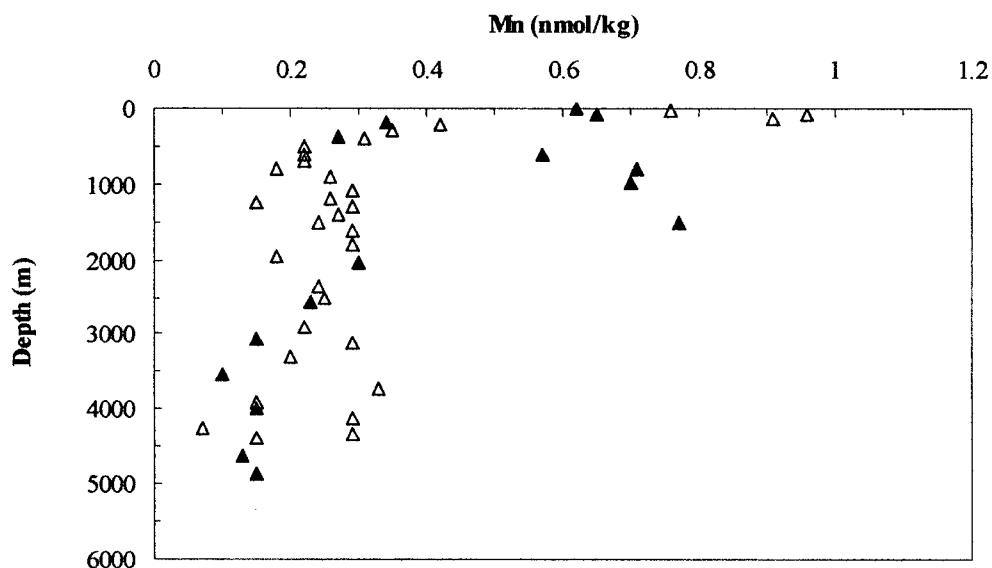
### 1.2.2 Manganese

Manganese (Mn), a second row transition element, is a scavenged or reactive type metal whose distribution is complicated by its redox chemistry. Mn occurs dissolved in seawater in the +2 oxidation state; it typically forms relatively weak complexes and exists predominantly in the marine environment as free hydrated  $\text{Mn}^{2+}$  or as  $\text{MnCl}^+$ . Mn(II) is thermodynamically unstable with respect to oxidation to insoluble manganese III and IV oxides, and concentrations based on calculations for the redox couples  $\text{MnO}_2$  or  $\text{MnOOH}$  with  $\text{Mn}^{2+}$  should be on the order of  $\text{pmol/kg}$  or less. However the relatively slow kinetics of  $\text{Mn}^{2+}$  oxidation in seawater prevent equilibrium from being attained and thus acts to set the mean concentration of dissolved Mn at a level higher ( $\text{nmol/kg}$ ) than that

predicted by oxidation. Mn(II) is very particle reactive and is scavenged throughout the water column on a time scale of approximately 10-100yr and is only significantly regenerated under reducing conditions. Estimates of Mn surface water residence time have been proposed by several groups. Statham and Burton (1986) suggested 5-10yr based on atmospheric input and an assumed solubility of 25% coupled with average surface water concentrations; Landing and Bruland (1987) suggested 19yr in the central Pacific, relative to offshore horizontal diffusion and using an advective model and surface mixed layer depth of 30m; Martin and Knauer (1984) derived 5yr using a model constrained by estimated atmospheric inputs, measured vertical fluxes and average concentrations; and Jickells *et al* (1994) suggested 5.4yr using atmospheric wet and dry deposition estimates for Mn in Bermuda and average surface water concentrations.

Many of the initial oceanographically consistent results regarding the marine Mn balance were obtained in the late 1970's by one laboratory (Bender, 1977; Klinkhammer, and Bender, 1980). Subsequent work included the distribution of Mn in the Pacific Ocean (see for example Landing and Bruland, 1980, 1987; Martin and Knauer, 1982, 1984; Jones and Murray, 1985; Bruland *et al*, 1994), the Indian Ocean (Saager *et al*, 1989; Lewis and Luther, 2000; Morley *et al*, 1992), the Sea of Japan (Shitashima and Tsubota, 1990), the Atlantic Ocean (Statham and Burton, 1986; Jickells *et al*, 1994; Shiller, 1997; Aballea *et al*, 1998; Yeats *et al*, 1992), the Southern Ocean (Sedwick *et al*, 1997, 2000), the Black Sea (Lewis and Landing, 1990), the East China Sea and the Yellow Sea (Minakawa *et al*, 1995). Representative profiles of dissolved Mn in the Atlantic and Pacific Oceans are shown in figure 1.2.2.1.

Several trends may be discerned from these studies. Open ocean surface water concentrations of dissolved Mn range from approximately 0.7-3.5nmol/kg in the Atlantic to approximately 0.5-3nmol/kg in the Pacific, to approximately 0.1-0.8nmol/kg in the Southern Ocean. Concentrations are supported through atmospheric deposition (Kremling, 1985) and photo-reductive dissolution of Mn oxyhydroxides (Sunda and Huntsman, 1988). Surface concentrations typically increase in coastal regions, where fluvial input (Jones and Murray, 1985) and remobilization from reducing shelf sediments are seen (Yeats *et al*, 1979; Johnson *et al*, 1992; Trefry and Presley, 1982).



**Figure 1.2.2.1 Mn versus depth in the Atlantic and Pacific Oceans.**

**(Legend: ▲=Pacific data; open ▲=Atlantic data)**

(Landing and Bruland, 1980; Statham *et al*, 1998)

Intense oxidative scavenging can remove Mn from the water column leading to decreasing concentrations with depth. Values are typically low and uniform ( $<0.5\text{nM}$ ) below the  $\text{O}_2$  minimum zone (Statham *et al*, 1988; Landing and Bruland, 1987). Several mechanisms have been proposed for the scavenging of Mn onto particles including microbial mediation (Trefry and Presley, 1982; Sunda and Huntsman, 1987; Tebo and Emerson, 1984); and/or passive scavenging onto the surface of biogenic or organically coated particles (Martin and Knauer, 1983). Removal of dissolved Mn to particulate phases is reflected in a concomitant increase the ratio of reactive (acetic acid leachable) to refractory particulate Mn in oxygenated deep waters (Landing and Bruland, 1987) and in particulate Mn/Al ratios above crustal values for areas affected by redox cycling.

Dissolved Mn maxima are observed at depths around 500-1500m in more intense  $\text{O}_2$  minimum zones (Landing and Bruland, 1980, 1987; Martin and Knauer, 1982, 1985). Following the discovery of these so called 'secondary' maxima, several mechanisms were proposed to account for their existence: release of soluble Mn(II) from organic matter as



it is consumed; reduction of Mn(IV) oxides in continental margin sediments that intersect the O<sub>2</sub> minimum followed by transport of dissolved Mn(II) into the ocean interior;; and reductive dissolution of Mn oxyhydroxides phases exported from the surface waters (Yeats, 1979; Martin and Knauer, 1984). The relative importance of each will depend on localized hydrodynamic conditions, distance from the shore and the strength of inputs to the surface.

Dissolved Mn maxima are also observed at around 2000-3000m due to hydrothermal input (Aballea *et al*, 1998; Massoth *et al*, 1999). Hydrothermal input of Mn is potentially the largest single source of Mn to the world's oceans. The concentration of dissolved Mn in a 350°C end-member hydrothermal fluid is estimated to be on the order of 1mmol/kg, significantly higher than that of surrounding seawater and the hydrothermal Mn signature may be observed many miles from the ridge crest before scavenging and mixing erode the signal.

#### 1.2.2.1 Profiles

Much of the initial work on Mn cycling in the marine environment focused upon the Pacific Ocean where vertical profiles are typically dominated by external sources leading to surface maxima, intermediate maxima associated with the O<sub>2</sub> minimum and intermediate/deep water maxima in regions subject to the influence of active hydrothermal vents and/or reducing sediments. Klinkhammer and Bender (1980), Landing and Bruland (1980, 1986), Martin and Knauer (1984), Jones and Murray (1985), and Martin *et al*, (1985) provided data from the North Pacific showing elevated surface layer values decreasing from 2-10nmol/kg nearshore to 0.6-1nmol/kg offshore. Slightly higher concentrations of 1-2nmol/kg were observed within the central gyre. Sources producing this surface maximum include fluvial input, diffusion and upwelling from reducing shelf sediments and atmospheric deposition. Klinkhammer and Bender (1980) favored eolian deposition as the dominant factor in the central gyre region, while Landing and Bruland (1980) determined an inverse relationship between atmospherically derived <sup>210</sup>Pb and Mn and thus suggested that riverine and sediment input overshadows any potential eolian source near ocean boundaries. Slightly higher dissolved Mn concentrations were observed in the North Pacific gyre relative to the South Pacific gyre

consistent with enhanced eolian and fluvial sources in the northern hemisphere. Horizontal gradients were observed in the O<sub>2</sub> minimum zone with Mn decreasing from 1.4-4.7nmol/kg near the continental slope to 0.5-0.7nmol/kg in open waters. Concentrations decreased with depth below the oxygen minimum depth to low and uniform values (<0.5nmol/kg). More recently, Bruland *et al* (1994) provided vertical data from the stratified central north Pacific showing elevated surface concentrations maintained by atmospheric deposition and photo-reduction of particulate Mn to dissolved Mn ranging from approximately 0.6-1.0nmol/kg. Scavenging to particulate phase caused concentrations to decrease through the seasonal thermocline to a pronounced minimum (approaching 0.1nmol/kg) at around 400m depth. A secondary maximum of about 0.45nmol/kg around the O<sub>2</sub> minimum was observed followed by decreasing values to less than 0.1nmol/kg within deep and near bottom waters. Minakawa *et al* (1998) extended the data set to include the Bering Sea and the northern North Pacific. Bering Sea concentrations were high in surface (1.7-4.7nmol/kg) and bottom waters (1.2-7.8nmol/kg) whilst levels were relatively low in intermediate waters. Both surface and bottom water concentration decreased with distance from the shelf. Northern North Pacific stations showed similar trends to those in the Bering Sea with high surface (1.3-2.9nmol/kg) and deep water (0.24-2.7nmol/kg) concentrations. High concentrations of more than 2nmol/kg were observed in the Aleutian Trench suggesting that Mn is supplied from the Trench slope. The lowest values were found in the Gulf of Alaska. Concentrations typically increased with proximity to the Bering Sea suggesting that waters outflowing from the Bering Sea basin are a significant source of Mn to the northern North Pacific.

Several laboratories have presented work from the Arabian Sea (northwestern Indian Ocean). This area is characterized by strong seasonal upwelling driven by the SW monsoons and a broad O<sub>2</sub> minimum zone in intermediate waters with O<sub>2</sub> concentrations as low as 1μM. Vertical profiles showed striking similarities to those of the east Pacific where a similar O<sub>2</sub> regime exists. Saager *et al* (1989), Morley *et al* (1992), Lewis *et al* (2000) and all reported a strong Mn maximum coincident with the O<sub>2</sub> minimum zone.

In the Atlantic Ocean, the distribution of Mn is primarily controlled by atmospheric input (Kremling, 1985; Statham and Burton, 1986), intense oxidative and

particle scavenging at mid-depth (Sunda and Huntsman, 1987, 1988; Tebo and Emerson, 1984) and fluxes from reducing shelf and slope sediments (Trefry and Presley, 1982; Heggie *et al*, 1987; Johnson *et al*, 1992) leading to surface enrichment and a decrease in concentration with depth.

Profiles for the western North Atlantic provided by Yeats and Brewers (1985), Jickells *et al* (1987), Yeats *et al* (1992) and Statham *et al* (1998) all showed high surface water values (up to ~4nmol/kg) and subsequent decreasing concentration with depth (0.1-0.25nmol/kg). Le Gall *et al* (1999) provided data from the shelf edge in the Celtic and Hebridean Seas. Mn surface concentrations decreased from shelf waters (maximum concentrations close to 6nM) to oceanic waters (around 0.5nM in the deepest stations) and with depth (0.1-0.5nM). In several areas high bottom water concentrations were observed (up to 0.85nM) suggesting flux from reducing shelf sediments.

Recently, Sedwick *et al* (1997, 2000) extended the Mn data set by presenting results from the Southern Ocean showing high surface water concentrations for stations over the continental slope (>2nM), while open ocean stations showed values between 0.09-0.5nM.

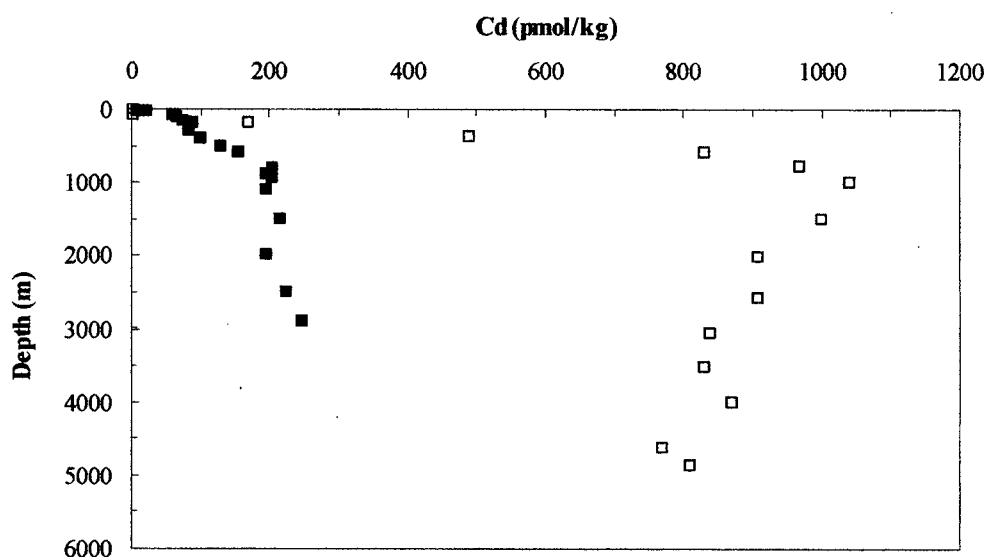
In summary, Mn is a scavenged or reactive type metal whose distribution is complicated by its redox chemistry. Concentrations are high at the surface and then decrease with depth as dissolved  $Mn^{2+}$  is sorbed onto sinking particles and removed to the sediments. If  $O_2$  concentrations are low, then a subsurface maximum is observed. Deep water concentrations are low in the absence of hydrothermal or other advective features. The major sources of Mn to surface waters are dust deposition and fluvial input and this produces significant variability in Mn profiles. Fluvial and sediment input both can play a significant role in coastal waters.

The average dissolved Mn concentration in the oceans is ~360pmol/kg with open ocean surface water concentrations up to ~3.5nmol/kg in the Atlantic, up to ~3nmol/kg in the Pacific, and up to ~0.8nmol/kg in the Southern Ocean. Mn has a relatively short residence time ranging from 5-19yr.

### 1.2.3 Cadmium

#### 1.2.3.1 Introduction

Cadmium (Cd) is a second row transition metal, directly below zinc in the periodic table. It is divalent in seawater and exists primarily as chloro-complexes. It is thought to be a non-essential element yet exhibits a nutrient type distribution showing surface water depletion and an increase with depth to a maximum coincident with that exhibited by the 'soft' nutrients, phosphate ( $\text{H}_2\text{PO}_4^-$ ) and nitrate ( $\text{NO}_3^-$ ). Representative profiles for Cd in the Pacific and Atlantic are shown in figure 1.2.3.1.1.



**Figure 1.2.3.1.1 Cd versus depth in the Atlantic and Pacific Oceans.**

**(Legend: ■= Atlantic data; □= Pacific data)**

(Bruland, 1980; Martin *et al*, 1993)

#### 1.2.3.2 Profiles

Some of the first profiles for Cd were presented by Martin *et al* (1976) from the eastern North Pacific. In the upper 100m Cd ranged from 0.03-0.06nmol/kg and closely co-varied with the labile nutrients. Bruland *et al* (1978) subsequently presented a more detailed examination of Cd in the California Current and in the eastern tropical Pacific,

reporting values ranging from 0.04nmol/kg in surface waters to maximum of 1.1nmol/kg at the depth of the phosphate and nitrate maxima. Again, a correlation with phosphate and nitrate was observed at all depths.

In 1980 Bruland extended and confirmed his earlier work by presenting data from the central North Pacific. Several authors have reported elevated Cd values coincident with coastal upwelling waters of the California Current including Bruland *et al* (1995) who observed values as high as 0.16nmol/kg off Santa Cruz, van Geen *et al* (1996) who reported values up to 0.6nmol/kg off central and northern California, and Sanudo-Wilhelmy *et al* (1996) who recorded values up to 0.6nmol/kg off Baja California.

In the Atlantic, Saager *et al* (1997), Yeats *et al* (1995), Danielsson *et al* (1985), Landing *et al* (1995) and Martin *et al* (1993) reported similar surface water values ranging from about 0.03-0.5nmol/kg and an increase with depth similar to phosphate and nitrate to a subsurface maximum at the depth of the nutrient maxima. Le Gall *et al* (1999) and Muller *et al* (1994) reported similar data for surface waters over the Hebridean Shelf, in the Celtic Sea, the North Sea, the English Channel and the Northeastern Atlantic (about 0.01-0.3nmol/kg).

Morley *et al* (1992) presented results from the southwestern Indian Ocean. The overall distribution conformed to those found in other oceans with very low values in surface waters (as low as 1pM) and an increase to a subsurface maximum coincident with the phosphate maximum; deep water concentrations (about 640pM) were intermediate between those for the North Atlantic and North Pacific Oceans. Saager *et al* (1991) also reported significant surface water depletion of dissolved Cd in the Northwest Indian Ocean with concentrations ranging from 80pM in waters overlying the upwelling zone of Oman to 8pM in waters of the central basin. Concentrations increased to a maximum (800-1100pM) at around 1200-1500m depth and then decreased toward the sea floor (about 650-1000pM).

In the Southern Ocean, Martin *et al* (1990), Westerlund and Ohman (1991), Frew (1995) and Nolting *et al* (1991, 1995) all reported similar high surface water Cd concentrations (about 0.28-0.68nmol/kg) coincident with high nutrient signals; this elevation was attributed to upwelling of deep water in combination with relatively low primary production; the low biological activity ensuring that Cd does not become

depleted in the surface water. For deeper waters, values varied from about 0.3-0.55nmol/kg for North Atlantic Deep water reported by Bruland and Franks (1983), to about 0.45-0.48nM for Antarctic Intermediate Water south of new Zealand reported by Frew *et al* (1992, 1995) to about 0.7-1nM for deep Antarctic waters reported by Nolting *et al* (1991), Orren and Monteiro (1985) and Martin *et al* (1990).

#### 1.2.3.3 The global Cd/P relationship

It is now well established that the concentration of Cd in the open ocean is closely related to biological activities and that its vertical distribution showing nutrient like depletion in surface waters and enrichment at depth is very similar to that of nitrate and phosphate (P) (Martin *et al*, 1976; Bruland, 1980; Frew and Hunter, 1992, 1995; Bruland and Franks, 1983; Boyle *et al*, 1976). Early studies suggested Cd as a close analogue of phosphate since the ratio of Cd and P concentrations in different regions of the global ocean displayed little variation, particularly when comparing North Pacific and North Atlantic data sets (Bruland, 1980; Bruland and Franks, 1983; Boyle *et al*, 1976). This presumably implies that Cd is taken up by phytoplankton in the surface layer in a relatively constant Redfield type ratio with respect to carbon and the micronutrients. However, as the quantity and quality of data sets increased, evidence mounted in support of two Cd/P relationships (Yeats *et al*, 1995; Frew and Hunter, 1992, 1995; de Barr *et al*, 1994; Frew, 1995). In deep waters the concentration of Cd at a given value of P is consistent within about  $\pm 7\%$ , but at  $P=1.3\mu\text{mol/kg}$  a significant slope change occurs with data above  $P=1.3\mu\text{mol/kg}$  dominated by the South Atlantic and Pacific and data below  $P=1.3\mu\text{mol/kg}$  dominated by the Atlantic and upper ocean. Several mechanisms have been proposed to explain this so called P 'kink': (1) an injection of low Cd/P sub Antarctic water to intermediate depths of the global ocean (Loscher *et al*, 1997); (2) remineralization of low Cd/P detritus from biota produced in waters formed at the subtropical convergence (Frew and Hunter, 1992) and (3) the formation of Antarctic Bottom water which has as a major component near surface waters which presumably would have a high Cd/P ratio (Frew, 1995). Recently Loscher *et al* (1997) provided new data from the Southern Ocean which attempted to fill a gap that existed between the North Atlantic and Indo-Pacific data. These authors again suggested a model with two

different relationships for the North Atlantic and the Indo-Pacific Ocean that deviated with statistical significance from a single global linear relationship. However it appears that further accurate Cd/P data are needed, particularly from low concentration areas, in order to conclusively determine the global Cd/P relationship. Finally, it is worth noting at this point, that the Cd/P relationship does not hold in surface waters to anywhere near the extent seen for deep waters. For example, Bruland (1980) found that Cd was depleted much earlier than P in coastal waters of the Pacific central gyre while Bruland and Franks (1983) and Kremling and Pohl (1983) observed opposite results on the US east coast and in the western European shelf.

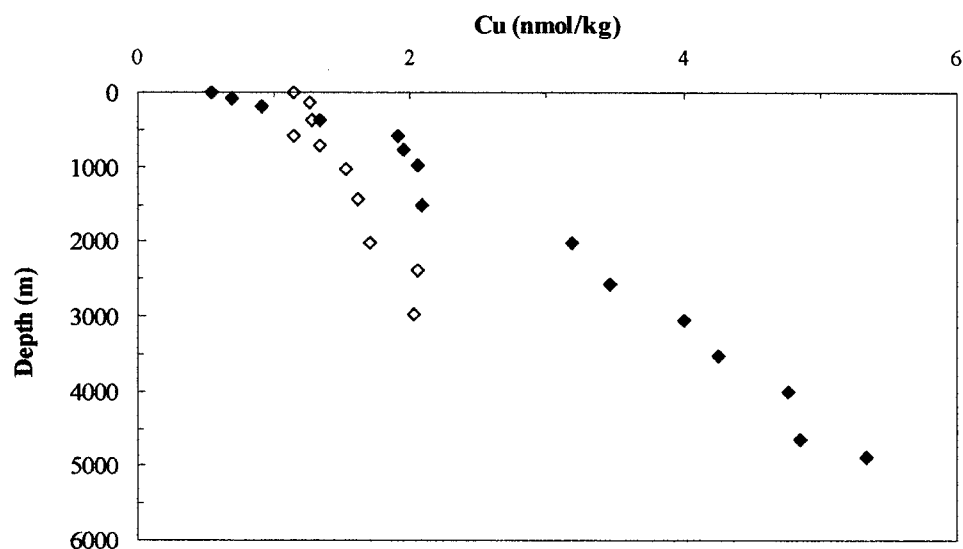
In summary, Cd exhibits a nutrient type profile with oceanic concentrations ranging from  $\sim 1$ -2 pmol/kg up to  $\sim 1.2$  nmol/kg. Its oceanic distribution is dominated by an involvement in a shallow regeneration cycle similar to P and  $\text{NO}_3^-$ . This leads to low surface water concentrations and increasing concentrations with depth to a maximum correlated to those of the 'soft' nutrients. Residence times for Cd are on the order of 50,000 yr (Bruland, 1980).

#### 1.2.4 Copper

Copper (Cu) is a first row transition metal and exists primarily in seawater as carbonato- and hydroxy- complexes, as the free hydrated ion, and in organic complexes. Its concentration in seawater ranges from 0.5-6 nmol/kg. Its oceanographic distribution is intermediate between that of a nutrient type element and that of a reactive type element, and reflects the influence of biological uptake, scavenging and bottom water sources. Vertical profiles typically show surface water depletion and a gradual increase in concentration toward bottom waters. Residence times for Cu have been reported to be approx. 1000 yr in deep waters (Boyle *et al*, 1977; Bruland, 1980; Bruland and Franks, 1983).

Boyle and Edmond (1975) presented some of the earliest work on Cu, studying the distribution of Cu in Pacific surface waters south of New Zealand. Subsequently, Boyle *et al* (1977) and Bruland (1980) extended this work to other areas of the Pacific. The vertical distribution of Cu in the Pacific is characterized by an approximately linear increase with depth, with profiles from the central Pacific gyre (Bruland and Franks,

1983) showing surface water depletion (0.4-0.5nmol/kg) and bottom water values as high as 5.3nmol/kg. The deviation from a nutrient type profile reflects *in situ* scavenging within deep waters and the bottom water maximum suggests substantial benthic input (Bruland and Franks, 1983). Values of 1.2nmol/kg were observed in surface waters of the California Current (Bruland, 1980) and surface water depletion was significantly less than that observed in the open ocean.



**Figure 1.2.4.1**  
**Cu versus depth in the Atlantic and Pacific Oceans.**  
**(Legend: ◆=Pacific data; ◇=Atlantic data)**  
**(Bruland and Franks,1983; Bruland, 1980)**

Many authors have reported data for the Atlantic. In the eastern Atlantic Ocean for example, Saager *et al* (1999) reported surface water concentrations ranging from 0.7-1.3nmol/kg and a deep water maximum indicative of a benthic source of around 1.2-3.1nmol/kg. Similar results from the eastern and central South Atlantic were obtained by



Yeats *et al* (1995); these authors reported surface water values up to about 1.5nmol/kg and a deep maximum of up to about 3nmol/kg. This maximum could not be explained solely in terms of mixing of southern source waters with high Cu concentration with lower concentration northern waters and again a significant bottom water source is suggested. Muller *et al* (1994) obtained surface water values up to 2nmol/l in the northeast Atlantic which was in good agreement with previous data from Kremling and Pohl (approx. 1.15nmol/kg) and Kremling (1985) (approx. 1.3nmol/kg). Similar results were also obtained by Bruland and Franks (1983), Jickells and Burton (1988) and Landing *et al* (1995) for various eastern Atlantic stations.

At high latitudes where lack of stratification causes ready mixing of deep and surface water, Cu concentrations similar to deep water values are observed. Westerlund and Ohman (1991) for example, reported 1.6-2.5nmol/kg for the Weddell Sea. van der Loeff *et al* (1996) and Le Gall *et al* (1999) reported concentrations of about 1-2nM in surface waters over the Hebridean Shelf and up to 3nM in surface waters over the Celtic Sea shelf. Loscher *et al* (1998) reported values as high as 2.2nM in the Southern Ocean.

In summary, Cu has a modified, nutrient type profile. It is depleted at the surface and then concentrations increase with depth. Cu does not show the typical nutrient mid-depth maximum. This behavior may be explained by the balance that exists between the remineralization of particulate Cu from sinking particles back to the dissolved phase and the subsequent re-scavenging of reactive Cu (II). Cu has a residence time of 1000 years (Boyle *et al*, 1977) and its average concentration in the ocean is ~2.4nmol/kg.

### 1.3 Research Objectives

The principle objective of this research is to gain an understanding of the impact and the relative importance of coastal sources on Mn, Al, Cd and Cu concentrations and distributions off the Pacific Northwest coast.

Coastal waters provide the link between the continents and the oceans. It is here that we observe the results of the complex biogeochemical cycling particular to coastal and estuarine environments. Fluvial runoff, sediment resuspension and diagenesis, coastal upwelling, estuarine mixing, scavenging, biological productivity and uptake all combine to significantly impact the distribution and concentration of trace metals. This

study investigates these sources and focuses in particular on input from reducing shelf sediments and input from the Columbia River.

Reducing shelf sediments may supply trace metals to overlying waters either by diffusion from pore waters and/or resuspension of sediments - this research will investigate the extent and impact of sediment supply particularly in light of the upwelling known to be occurring at the time of sampling. In addition, the bathymetry of the Pacific coastline, with its significant variations in continental shelf width, allows interpretation of the impact of shelf sediments on the supply of trace metals in upwelled waters.

Mn, Al and Cd are known to have fluvial sources and many authors have reported increased concentrations coincident with low salinity waters in various regions of the global marine environment. This research will investigate whether the Columbia is a significant source of Mn, Al and Cd to surface waters, and if so the subsequent behavior of the dissolved metals as they are transported offshore.

Chapter One thus presents an introduction to the research. Chapter Two details the development and modification of an existing technique to measure dissolved Mn, Al, Cd and Cu from a seawater matrix. Chapters Three and Four are written as publications and may necessarily include some repetition. Both chapters contain detailed information on the marine environment being studied. Chapter Three examines the impact of upwelling and sediment sources on trace metal concentrations. Chapter Four examines the impact of the Columbia River and also contains a comparison of the behavior of Al and Ga from the study region. And Chapter Five discusses conclusions arising from this work.

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## **Chapter 2: Method Development**

### **2.1 Introduction**

This chapter details the modification of an existing technique for the measurement of trace metals using chelex pre-concentration followed by graphite furnace atomic absorption spectroscopy (GFAAS). The elements successfully analyzed using this system were Mn, Al, Cd and Cu.

### **2.2 Instrumentation**

#### **2.2.1 Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)**

Dissolved Mn, Al, Cd and Cu were determined by GFAAS, using a Varian Spectra AA300 with Zeeman background correction. GFAAS measures the absorbance of a vaporized and atomized sample injected into a platform graphite tube. External standards are utilized to build linear calibration curves from which metal concentrations are derived. Instrumental parameters used were modified from those suggested by the manufacturer and are shown in table 2.2.1.1, 2.2.1.2, 2.2.1.3, and 2.2.1.4. GFAAS is a single element technique, it is a highly specific method as atomic absorption lines are extremely narrow and electronic transition energies are unique for each element. Detection limits are low for many elements and the method is relatively low cost.

**Table 2.2.1.1 GFAAS Operation Conditions for Mn**

| Description         |  | Conditions |            |          |
|---------------------|--|------------|------------|----------|
| Instrument mode     |  | Absorbance |            |          |
| Measurement mode    |  | Peak Area  |            |          |
| Lamp current        |  | 5mA        |            |          |
| Bandwidth           |  | 0.2nm      |            |          |
| Wavelength          |  | 279.5nm    |            |          |
| Sample introduction |  | Automixing |            |          |
| Furnace parameters  |  | Temp       | Total Time | Gas Flow |
| Step No.            |  | (°C)       | (sec.)     | (L/min)  |
| 1                   |  | 85         | 5          | 3        |
| 2                   |  | 95         | 40         | 3        |
| 3                   |  | 120        | 10         | 3        |
| 4                   |  | 700        | 5          | 3        |
| 5                   |  | 700        | 1          | 3        |
| 6                   |  | 700        | 2          | 0        |
| 7                   |  | 2400       | 3.1        | 0        |
| 8                   |  | 2400       | 2          | 3        |

**Table 2.2.1.2 GFAAS Operation Conditions for Al**

| Description                    |  | Conditions   |                      |                     |
|--------------------------------|--|--------------|----------------------|---------------------|
| Instrument mode                |  | Absorbance   |                      |                     |
| Measurement mode               |  | Peak Area    |                      |                     |
| Lamp current                   |  | 4mA          |                      |                     |
| Bandwidth                      |  | 0.5nm        |                      |                     |
| Wavelength                     |  | 328.1nm      |                      |                     |
| Sample introduction            |  | Automixing   |                      |                     |
| Furnace parameters<br>Step No. |  | Temp<br>(°C) | Total Time<br>(sec.) | Gas Flow<br>(L/min) |
| 1                              |  | 85           | 5                    | 3                   |
| 2                              |  | 95           | 40                   | 3                   |
| 3                              |  | 120          | 10                   | 3                   |
| 4                              |  | 400          | 5                    | 3                   |
| 5                              |  | 400          | 1                    | 3                   |
| 6                              |  | 400          | 2                    | 0                   |
| 7                              |  | 2700         | 6.0                  | 0                   |

**Table 2.2.1.3 GFAAS Operation Conditions for Cd**

| Description         |  | Conditions |            |          |
|---------------------|--|------------|------------|----------|
| Instrument mode     |  | Absorbance |            |          |
| Measurement mode    |  | Peak Area  |            |          |
| Lamp current        |  | 4mA        |            |          |
| Bandwidth           |  | 0.5nm      |            |          |
| Wavelength          |  | 228.8nm    |            |          |
| Sample introduction |  | Automixing |            |          |
| Furnace parameters  |  | Temp       | Total Time | Gas Flow |
| Step No.            |  | (°C)       | (sec.)     | (L/min)  |
| 1                   |  | 85         | 5          | 3        |
| 2                   |  | 95         | 40         | 3        |
| 3                   |  | 120        | 10         | 3        |
| 4                   |  | 250        | 5          | 3        |
| 5                   |  | 250        | 1          | 3        |
| 6                   |  | 1800       | 4.8        | 0        |
| 7                   |  | 1800       | 2          | 3        |

**Table 2.2.1.4 GFAAS Operation Conditions for Cu**

| Description         | Conditions |            |          |
|---------------------|------------|------------|----------|
| Instrument mode     | Absorbance |            |          |
| Measurement mode    | Peak Area  |            |          |
| Lamp current        | 4mA        |            |          |
| Bandwidth           | 0.5nm      |            |          |
| Wavelength          | 327.4nm    |            |          |
| Sample introduction | Automixing |            |          |
| Furnace parameters  | Temp       | Total Time | Gas Flow |
| Step No.            | (°C)       | (sec.)     | (L/min)  |
| 1                   | 85         | 5          | 3        |
| 2                   | 95         | 40         | 3        |
| 3                   | 120        | 10         | 3        |
| 4                   | 800        | 5          | 3        |
| 5                   | 800        | 1          | 3        |
| 6                   | 800        | 2          | 0        |
| 7                   | 2300       | 3.1        | 0        |
| 8                   | 2300       | 2          | 3        |

### 2.2.2 Pumps

A Masterflex L/S Multi channel Cartridge pump (Cole-palmer Instrument Co.; Chicago, USA) equipped with an eight channel, 3-roller pump head was used to pump the samples through the resin during the pre-concentration step. FEP tubing (Labcor; Anjou, Canada) and C-Flex (a fluoro-elastomer) completed the pumping set-up. This set-up allowed eight samples to be pumped simultaneously. Flow rates were determined by weighing the amount of DDW pumped through the columns over a 10-minute period.

### 2.2.3 Others

An analytical balance with the precision of  $\pm 0.001\text{g}$  (Mettler PM1200, Fisher Scientific, Vancouver, Canada) was used to determine the weight of seawater, eluents and reagents.

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

## 2.3 Materials and Reagents

### 2.3.1 Resins

Several resins were utilized in this study:

(1) Analytical Grade Chelex-100 resin (100-200 mesh), a polystyrene-divinyl benzene co-polymer with an iminodiacetate functional group, was purchased from Bio-Rad Laboratories, Richmond, USA. This was used to preconcentrate trace metals from seawater.

(2) Toyopearl HW-40EC and HW75F resins, (ethylene glycol/methacrylate co-polymer based resins) and AF-Chelate-650M and AF-Epoxy-650M (same backbone as previous resins but with iminodiacetate and epoxy functional groups respectively) were purchased from TosoHaas, Montgomeryville, USA. Toyopearl was used for the synthesis of various 8 hydroxy-quinoline resins.

Resins used for pre-concentration purposes were initially cleaned with 2N  $\text{HNO}_3$  (nitric acid) (environmental grade) for five days and then with 2N Q- $\text{HNO}_3$  (ultra-clean nitric acid) for three days. Following loading onto the column the resin was further cleaned through the gravity addition of 60mL 2N Q- $\text{HNO}_3$ .

### 2.3.2 Acids, Bases and Buffers

Ultra clean acetic acid (Q-AcOH) and ultra clean ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) (both subjected to double sub-boiling distillation in a quartz or Teflon still by Seastar Chemicals Inc., Sidney, BC, Canada) were used to prepare ammonium acetate buffer



solution (0.3M). This was used to adjust the pH of seawater samples and to rinse and pH-adjust chelex-100 columns.

Ultra clean acetic acid (Q-CH<sub>3</sub>COOH) was used to pH-adjust seawater samples prior to the pre-concentration procedure. Analytical reagent grade hydrochloric acid (BDH Inc. Toronto, Ontario, Canada) was used to clean polyethylene bottles, AA sample cups, column parts, and pipette tips (see section 2.4.4. for full details of the cleaning procedure). Environmental grade nitric acid (68-71% prepared by Anachemia Science Division of Anachemic Canada Inc.) was used to clean polyethylene bottles, AA sample cups, column parts and pipette tips. Ultra clean nitric acid (Q-HNO<sub>3</sub>) (double sub-boiling distilled in a quartz or Teflon still by Seastar Chemicals Inc., Sidney, BC, Canada) was used to prepare 2.0 N HNO<sub>3</sub> for cleaning and eluting the chelex-100 columns.

#### 2.3.3 Distilled Deionized Water (DDW)

Water distilled with a Barnstead system (Barnstead/Thermolyn Corporation, Dubuque, Iowa) was then passed through a "Milli-Q" deionization system (Millipore Waters Associates, Milford, USA) in the laboratory at UBC, in the Department of Earth and Ocean Sciences.

#### 2.3.4 Metal Standards

Mn and Al standard solutions were prepared by successive dilution of 1000 mg/L single element certified atomic absorption standards (Delta Scientific, Mississauga, Canada) with 2N Q-HNO<sub>3</sub>.

#### 2.3.5 Reference Materials (CASS-3 and NASS-3)

The Nearshore Reference Material (CASS-3) and the Open Ocean Seawater Reference Material (NASS-3), filtered, stored and acidified, were purchased from the National Research Council of Canada (Ottawa, Canada), and used to determine the accuracy of the method.

### 2.3.6 Storage Bottles

All materials and solutions were stored in high density polyethylene bottles purchased from VWR Canlab, Mississauga, Canada. Polyprep disposable chromatography columns were obtained from BioRad laboratories (Richmond, USA). The columns are equipped with a porous polymer bed support and hold up to 2ml of resin in addition to 10ml eluent or sample in an integral reservoir.

## 2.4 Methods

### 2.4.1 Study Area

Seawater samples were collected during June/July 1997 on board the R/V "Point Sur". Ten horizontal transects, in which the ship initially traveled southeast (dog-leg) before traveling offshore, were determined. The study area extended from Big Sur in southern California to the Olympic Peninsula in Northern Washington.

### 2.4.2 Seawater Collection and Storage

Seawater samples were obtained by Professor Kristin Orians from the Department of Earth and Ocean Sciences at UBC using clean sampling procedures developed by Bruland *et al* (1979). Samples were collected using a trace-metal clean Teflon pump system. The intake tubing was towed at the front end of the ship at 1-2m depth. The pumped seawater was filtered using an acid-cleaned 0.45 $\mu$ m polypropylene cartridge filter and then acidified to pH2 with Q-HCl. Note that the 0.45 $\mu$ m filter size is an operationally chosen parameter and that all material that passes through this filter is termed 'dissolved'. All onboard sample collection, handling and storage were carried out in a clean area constructed inside the ship's dry lab from polyethylene sheets. Filtered air was supplied via a portable high efficiency particle air (HEPA) unit. Acidified samples were transported to a shore based laboratory and stored away from light for 1.5yr prior to analysis.

### 2.4.3 Temperature, Salinity, Chlorophyll-a and Nutrient Data

Temperature, salinity, chlorophyll-a and nutrient measurements were determined by members of the Bruland Research Group at the Institute of Marine Sciences, University of California at Santa Cruz. Seawater temperature and salinity data was acquired via the ship's flow-through SAIL loop system. Nutrient ( $\text{NO}_3^-$  and  $\text{H}_4\text{SiO}_4$ ) data was initially determined at sea with an autoanalyser, and also from frozen samples analyzed onshore at UCSC. Chlorophyll-a was determined fluorometrically at sea on samples vacuum filtered onto polycarbonate filters and extracted in 90% acetone according to methods developed by Parsons *et al* (1984).

### 2.4.4 Material Pre-Clean Treatment

All plastic-ware used in the study was subject to a clean treatment prior to use in order to remove any possible contaminants. The treatment involves initially rinsing (3x) with DDI, rinsing (3x) with acetone, rinsing (3x) with DDW and then soaking in 4N reagent grade HCl at 60°C for 48 hours. The plastic-ware is then rinsed again with DDW (3x) and soaked in 0.1N environmental grade  $\text{HNO}_3$  for a minimum of 1 week.

## 2.5 Method Development

The optimum conditions for the pre-concentration of Mn, Al, Cd and Cu from seawater were determined using the recoveries of metal spikes added to a seawater matrix. The spike, (10nmol/kg for Mn, 1nmol/kg for Al, 1nmol/kg for Cd and 2.5nmol/kg for Cu), was added to clean seawater (from station P where trace metal concentrations are known to be low) which had been stored at pH 2. A series of seawater "blanks" which contained the same amount of reagents but no added metal spikes were run along side the spiked samples. The following factors were investigated: resin choice, sample pH, resin volume, and pump flow rate.

### 2.5.1 Resins

At the heart of this procedure lies the chelating/ion-exchange resin. Ideally the resin should demonstrate great selectivity, rapid-exchange kinetics, high capacity, good

mechanical strength and stability at various pHs. Several resins were investigated during this study.

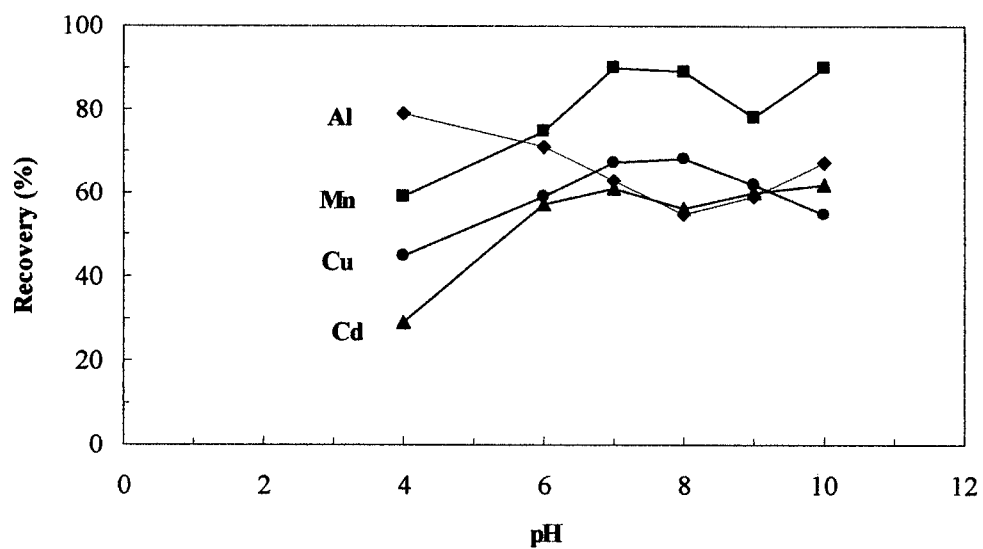
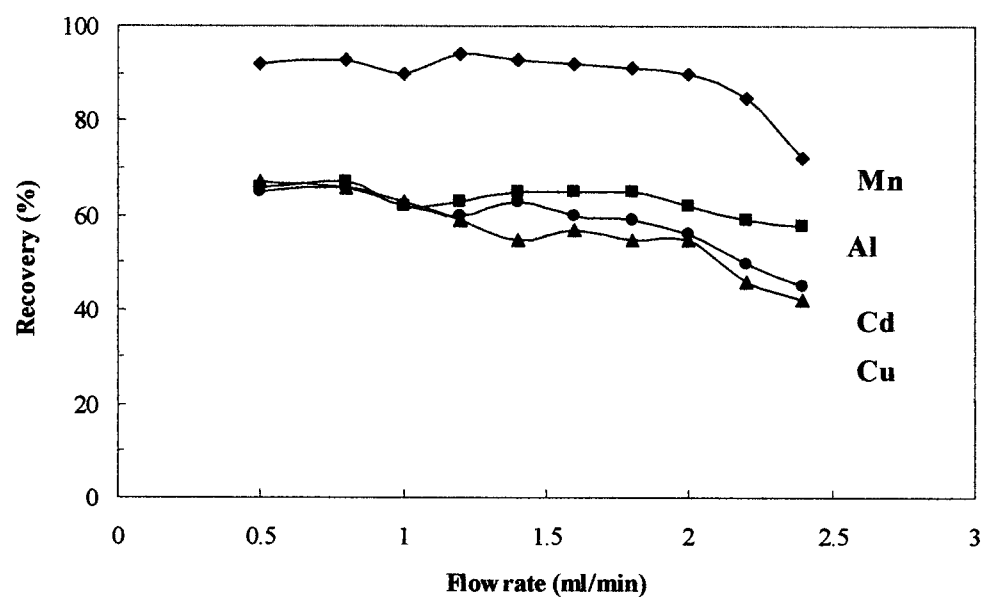
#### 2.5.1.1 Chelex-100

Chelex-100 is one of the most commonly utilized chelating resins for the removal of trace metals from seawater. It consists of an imminodiacetate functional group immobilized onto a styrene/divinylbenzene substrate. It displays high selectivity for polyvalent metals over more commonly occurring monovalent cations such as  $\text{Na}^+$  and  $\text{K}^+$ , has a high capacity, and is readily available commercially. However, Chelex-100 has a number of disadvantages; it has very slow exchange kinetics due to the hydrophobic nature of its solid support which results in slow pumping times; and this resin shrinks and swells with changing pH which prevents the use of miniature columns.

#### 2.5.1.2 AG-Chelate-650M

This resin, supplied by BioRad, consists of semi-rigid beads synthesized by a copolymerization of ethylene glycol and methacrylate type polymers. Its functional group is the imminodiacetate group. The presence of ether and hydroxyl groups at its surface ensures that the resin is highly hydrophilic in nature.

The recoveries of Mn, Al, Cd and Cu using this resin were tested at a variety of pHs and flow rates (figure 2.5.1.2.1). Recoveries were good (>90%) for Mn at flow rates between 0.8-2g/min but fairly poor for the other three metals (~55-67% between 0.8-2g/min). Recoveries for all metals decreased outside this range. Further problems were encountered with pH changes. The metals did not respond equally well to the same pH, which meant that if this resin were to be chosen a 'compromise' pH value (probably pH 7) would have to be selected.



**Figure 2.5.1.2.1** Metal recoveries of spiked standards using AG-Chelate-650M  
a) at various flow rates (pH=7) and b) at various pH's (flow rate=1.0ml/min)

#### 2.5.1.3 8-Hydroxyquinoline resins

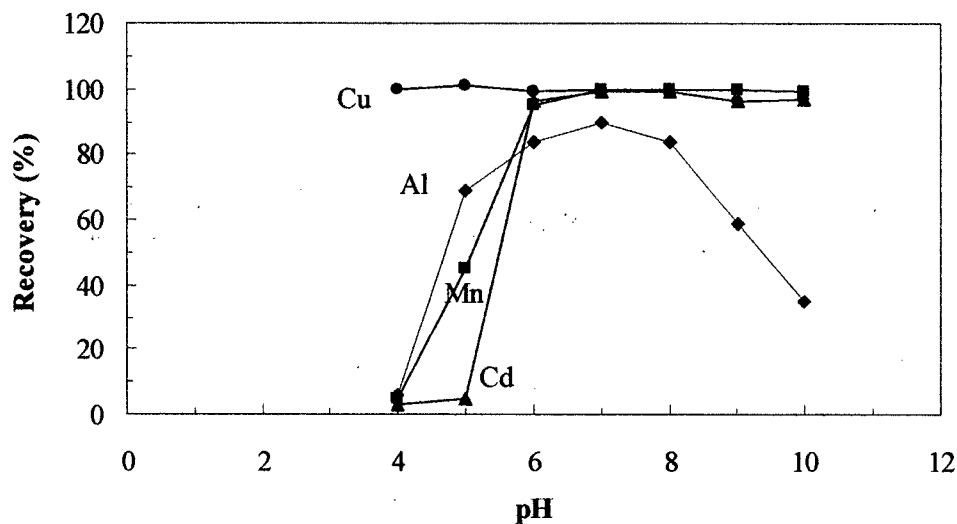
8-HQ, bound to either silica or a stable organic polymer matrix, has been extensively used to extract first row transition elements from aquatic samples (Akatsuka *et al*, 1992; Landing *et al*, 1986). One of the major advantages enjoyed by these resins is the significantly greater selectivity shown for transition elements versus alkaline earths. For example, Orians and Boyle (1993) used TSK-8HQ to successfully extract titanium (an element which is heavily interfered by calcium when using mass spectrometric detection) from seawater. Many attempts were made to synthesize this resin; however the synthesis proved time consuming and often failed for unknown reasons. The limited quantity of resin I did manage to synthesize had a very poor capacity (3-4 $\mu$ mol Cu/g resin as opposed to 100 $\mu$ mol Cu/g for Chelex-100).

I also investigated an alternative synthesis (Dierssen *et al*, 20001) in which 8-HQ is covalently bonded via a secondary amino-acid to the polymer substrate resin. In this case, an epoxide (epiclorohydrin) is used to initiate attack on the resin support hydroxyl group. Subsequent reaction with para-phenylenediamine provides the secondary amino acid. This synthesis was successful and resulted in a resin with good capacity (>100 $\mu$ mol Cu/g resin); however the starting materials were prohibitively expensive rendering the resin more suited to small-scale applications such as miniature columns found in on-line systems.

#### 2.5.2 pH (figure 2.5.2.1)

Sample pH was adjusted to values between 4 and 10 through the addition of  $\text{NH}_4\text{OH}$  and  $\text{AcOH}$ . The samples (100g) were then subject to the general pre-concentration procedure. A flow rate of 1.0ml/min was used for this study.

100% recoveries were obtained for Mn, Cd and Cu at pH values between 7.0 and 8.0. For the same pH range Al showed recoveries ranging from 84-90%. A value of pH  $7\pm 0.2$  was chosen for this study.



**Figure 2.5.2.1 Recovery Study at Various pH (flow rate=1.0ml/min)**  
**(Legend: ▲=Cd, ◆=Al, ■=Mn, ●=Cu)**

### 2.5.3 Volume of Chelex-100 Resin (table 2.6.2.1)

The effect of resin volume on metal recovery was investigated. For this study pH=7, flow rate = 0.5ml/min and 100g of sample were used. Recoveries were at or close to 100% in the range of 2.5ml to 4ml fresh resin for Mn, Cd and Cu and high (87-91%) for Al. Larger volumes were not investigated due to the inconvenience of the resulting longer sample run time. Smaller volumes (1.5ml and 2ml) resulted in lower recoveries. For this study a resin volume of 3ml was chosen to maximize convenience, and to minimize cost, column blanks and the possibility of capacity breakthrough.

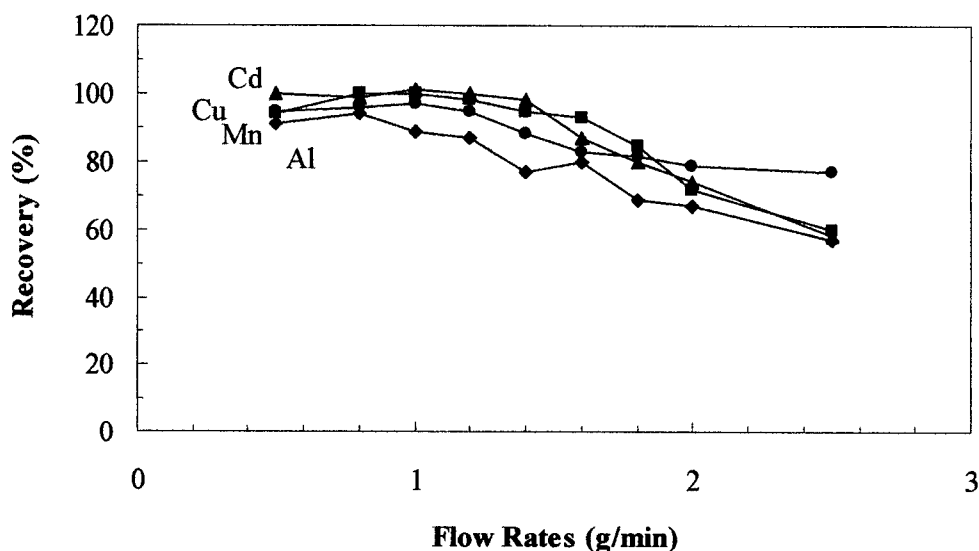
**Table 2.5.2.1 Effect of Resin Volume on Metal Recoveries**

| Volume of Chelex-100 resin<br>(ml) | Recoveries |           |           |           |
|------------------------------------|------------|-----------|-----------|-----------|
|                                    | Mn<br>(%)  | Al<br>(%) | Cd<br>(%) | Cu<br>(%) |
| 1.5                                | 83         | 62        | 79        | 88        |
| 2                                  | 90         | 68        | 89        | 86        |
| 2.5                                | 100        | 87        | 100       | 99        |
| 3                                  | 100        | 91        | 100       | 100       |
| 4                                  | 100        | 90        | 99        | 99        |
| 5                                  | 92         | 90        | 97        | 99        |

#### 2.5.4 Flow Rate (figure 2.5.4.1)

The effect of flow rate on metal recovery from seawater was investigated. Our pump system could not pump any slower than 0.5ml per minute so I initially chose to look at a flow rate range from 0.5-2.5ml. This study was carried at pH=7 and involved the use of 100g of sample. Results indicate that optimal recoveries are obtained from slow pumping. Mn, Cd and Cu show 100% or near 100% recovery at flow rates between 0.8 and 1.0ml/minute. Al shows recoveries around 80-90% for the same range of rates. For this study a flow rate of 0.8ml/minute was chosen.





**Figure 2.5.4.1 Recovery Study at Various Flow Rates (pH=7)**  
**(Legend: ▲=Cd, ◆=Al, ■=Mn, ●=Cu)**

#### 2.5.5 Eluent Concentration and Volume

The effect of eluent ( $\text{HNO}_3$ ) strength (1.6N-2.4N) and volume 2ml-12ml) on recovery was investigated. The study involved the use of 100g sample, a flow rate of 0.8ml/min and pH=7. All metals showed quantitative recovery for  $\text{HNO}_3$  concentrations between 1.6-2.4N and for eluent volume between 7-11ml. For this study a concentration of 2N and a volume of 8ml were chosen for the eluent.

#### 2.5.6 Sample Processing General Procedure

The general procedure utilized to determine Mn, Al, Cu and Cd was modified from an existing procedure developed by Yang (1993). All sample processing was performed in a trace metal clean laboratory (high efficiency pure air - HEPA, positive air pressure supply). Prior to use, acid cleaned PolyPrep columns containing 3ml Chelex-100 resin were cleaned with 6ml 2.0N  $\text{HNO}_3$  under gravity elution. The columns were rinsed with 10ml DDW and then pH adjusted to pH 7 with  $\text{NH}_4\text{Ac}$ . The resin was then shaken vigorously and resuspended. Filtered acidified seawater samples (100-125g) were

measured by weight. The samples were pH adjusted using  $\text{NH}_4\text{OH}$  and  $\text{AcOH}$  to pH 7. The samples were then pumped through the column at a flow rate of 0.8ml/minute. The columns were rinsed under gravity with 8x1ml  $\text{NH}_4\text{Ac}$  (0.3M) and 5x1ml DDW both at pH 7, and then eluted under gravity into 8ml acid washed polyethylene bottles with 8 x1ml 2N  $\text{HNO}_3$ . A spiked sample was run with every batch of six samples in order to check recoveries. Column eluents were analyzed on the GFAAS immediately or sealed, stored at room temperature, and analyzed at a later date. Analytical blanks were analyzed in the same manner except that 100ml DDW was used instead of seawater. The CASS-3 and NASS-3 standard reference materials were analyzed in the same manner as the seawater samples at a pH of 7.

## 2.6 Analytical Figures of Merit

### 2.6.1 Recovery Tests

Column recoveries were determined by spiking seawater (from Station 'P') with known amounts of Mn, Al, Cd and Cu and then subjecting these samples to the complete pre-concentration procedure. The difference between spiked and un-spiked seawater samples allowed the recoveries to be determined. Two replicates for each column were analyzed (table 2.6.1.1).

**Table 2.6.1.1 Mn Recoveries from Seawater Matrix at pH 7.0**

| Column Number  | Sample 1 | Sample 2 |
|----------------|----------|----------|
| 1              | 98       | 99       |
| 2              | 99       | 96       |
| 3              | 97       | 99       |
| 4              | 100      | 100      |
| 5              | 101      | 99       |
| 6              | 100      | 99       |
| 7              | 99       | 98       |
| 8              | 100      | 99       |
| Average        | 99       | 98.6     |
| Std. Deviation | 1.3      | 1.2      |

**Table 2.6.1.2 Al Recoveries from Seawater Matrix at pH 7.0**

| Column Number  | Sample 1 | Sample 2 |
|----------------|----------|----------|
| 1              | 85       | 84       |
| 2              | 87       | 88       |
| 3              | 89       | 88       |
| 4              | 85       | 86       |
| 5              | 87       | 84       |
| 6              | 87       | 86       |
| 7              | 86       | 85       |
| 8              | 89       | 90       |
| Average        | 87       | 86.4     |
| Std. Deviation | 1.6      | 2.1      |

**Table 2.6.1.3 Cd Recoveries from Seawater Matrix at pH 7.0**

| Column Number  | Sample 1 | Sample 2 |
|----------------|----------|----------|
| 1              | 99       | 100      |
| 2              | 95       | 101      |
| 3              | 99       | 100      |
| 4              | 100      | 98       |
| 5              | 98       | 99       |
| 6              | 100      | 98       |
| 7              | 101      | 99       |
| 8              | 101      | 100      |
| Average        | 99       | 99.4     |
| Std. Deviation | 1.9      | 1.1      |

**Table 2.6.1.4 Cu Recoveries from Seawater Matrix at pH 7.0**

| Column Number  | Sample 1 | Sample 2 |
|----------------|----------|----------|
| 1              | 93       | 100      |
| 2              | 94       | 101      |
| 3              | 99       | 100      |
| 4              | 100      | 99       |
| 5              | 98       | 99       |
| 6              | 100      | 98       |
| 7              | 101      | 99       |
| 8              | 101      | 100      |
| Average        | 98       | 99       |
| Std. Deviation | 3.1      | 0.92     |

Throughout the actual sampling determination procedure a spiked sample was run with every batch of six samples in order to check recoveries.

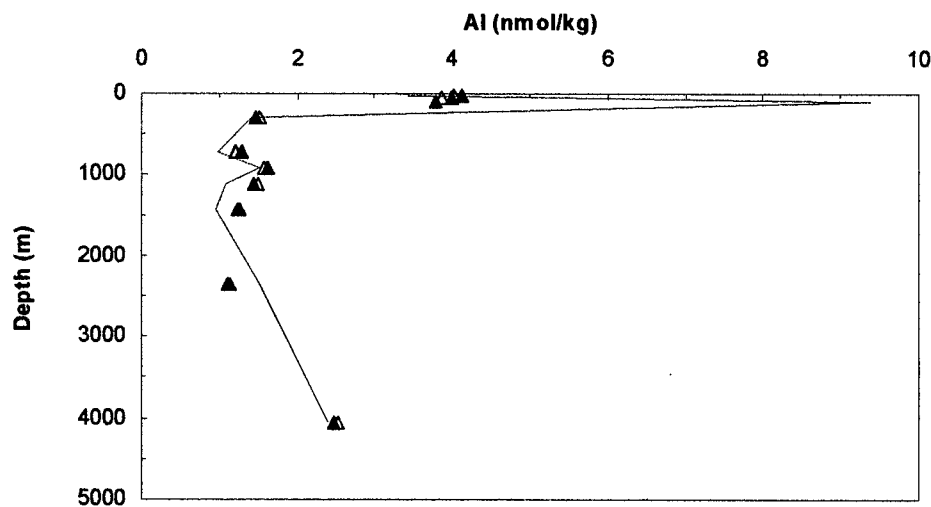
#### 2.6.2 Accuracy and Precision

The accuracy of this method was assessed through analysis of dissolved Mn, Cd and Cu in seawater reference standards from the National Research Council of Canada. The reference seawater sample used was the Open Seawater Reference Material (NASS-3). Triplicate measurements of NASS-3 were determined. Using Student's t-test, the data show no significant differences between the found and certified results for these metals at the 95% confidence limit.

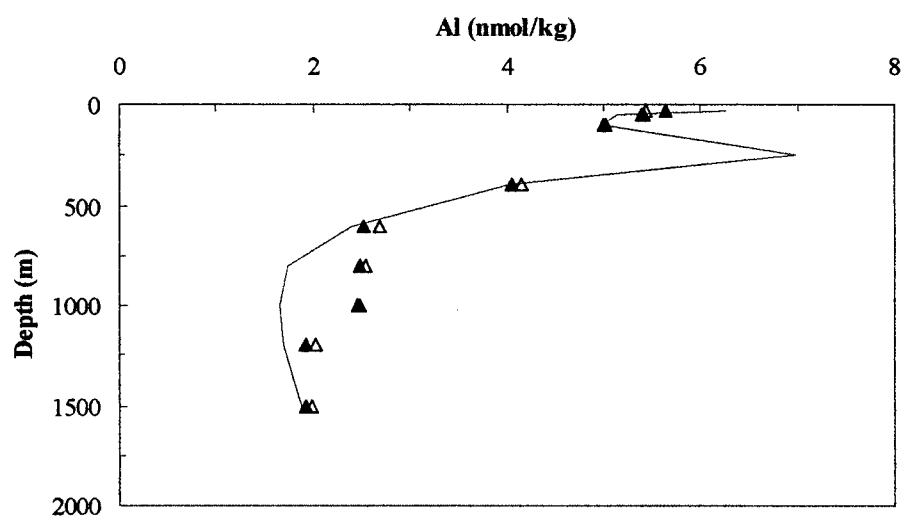
**Table 2.6.2.1 Found and Certified Values for Seawater Standards**

| Element | NASS-3 certified<br>(ng/l) | NASS-3 found<br>(ng/l) |
|---------|----------------------------|------------------------|
| Mn      | 31 ± 12                    | 28 ± 1                 |
| Cd      | 22 ± 4                     | 28 ± 3                 |
| Cu      | 93 ± 9                     | 87 ± 15                |

As no certified reference material was available for Al, the accuracy of the method was evaluated through comparison with results obtained by Yang (1993) for samples from the Western North Pacific. Yang (1993) obtained her data through pre-concentration of the seawater matrix using Chelex-100 resin and subsequent ICP-MS detection. While my data do not agree perfectly with Yang's in terms of absolute values, they do show good agreement with most of Yang's trends (figure 2.6.2.1-2.6.2.3). The disagreement between my values and those of Yang's can be explained by a number of factors. Yang's samples had been stored for 4 years prior to my analysis in less than ideal conditions; and it is possible that evaporation and/or contamination had occurred to some extent. However, Yang's original data were somewhat anomalous in that they did not completely reflect the expected trend for Al in this area of the ocean. For example, Yang's data show a sub-surface Al maximum in contrast to the surface maximum observed by Oriens and Bruland (1986) and Yang's intermediate water values are higher than those observed by Oriens and Bruland (1986). It is possible that this deviation resulted from some kind of analytical error. While I would have preferred to evaluate my method against a more reliable sample set, the good agreement between the 2 samples I determined for each station and the high precision of the method for Al (see section below) led me to conclude that my method was rigorous.



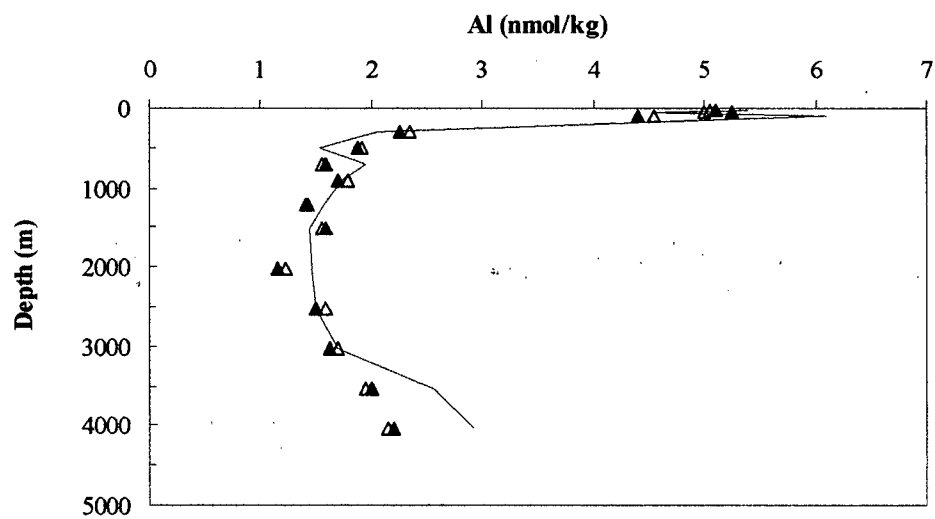
**Figure 2.6.2.1 Al distributions for Station HS13, Western North Pacific**  
(Legend: Line = Yang (1993) data; open and closed  $\blacktriangle$  = data from this study)



**Figure 2.6.2.2**

**Al distributions for Station HS14, Western North Pacific**

**(Legend: Line = Yang (1993) data; open and closed ▲ = data from this study)**



**Figure 2.6.2.3**

**Al distributions for Station HS15, Western North Pacific**

**(Legend: Line = Yang (1993) data; open and closed ▲ = data from this study)**

Analytical precision for this method was evaluated by examining the relative standard deviations (RSDs) determined for 10 replicate analyses on the NASS-3 seawater standard. The RSDs were between 4 and 13% for all elements.

### 2.6.3 Limits of Detection

Two types of blanks were determined; a procedural blank and a column blank. The procedural blank was obtained by subjecting blanks (DDW) to the preconcentration procedure described previously. This procedure was then compared to column blanks involving only the acid elution of a cleaned column. The column blank ensured that the procedural blank was not overestimated due to possible contamination of DDW. Analysis of both blanks yielded nearly identical levels of all trace metals indicating that the resin was the most significant source of metal contamination.

Detection limits for each element are shown below. These limits were calculated based on three times the standard deviation of eight process blanks.

**Table 2.6.3.1 Process Detection Limits for Mn, Cd, Al and Cu**

| Element | Detection Limits<br>(nmol/kg) |
|---------|-------------------------------|
| Mn      | 0.08                          |
| Cd      | 0.004                         |
| Al      | 0.07                          |
| Cu      | 0.09                          |

## 2.7 References

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## **Chapter 3**

### **Oceanic and Benthic Sources of Dissolved Mn, Al, Cd and Cu to NE Pacific Coastal Waters**

#### **3.1 Introduction**

The ocean margin (which includes estuaries, the continental shelf, and slope) is the critical interface between land and ocean, and is impacted by several sources that may significantly affect trace metal distributions. Possible sources are fluvial, atmospheric, oceanic (surface currents, eddies, upwelling) and benthic (sediment). This chapter focuses upon the impact of oceanic and benthic sources on distributions of dissolved Mn, Al, Cd, and Cu in NE Pacific coastal waters. Sections 3.2 and 3.4 explain how upwelling and the sediments can act as sources of trace metals, section 3.3 describes the setting for this study, section 3.5 gives examples of prior work citing upwelling and sediments as sources of Mn, Al, Cd and Cu; 3.6 describes results from this research; section 3.7 discusses the results; and section 3.8 summarizes findings.

#### **3.2 Upwelling**

Upwelling may be defined as a circulation pattern in which deeper water (from <100m for coastal upwelling to ~200-300m for equatorial upwelling) is transported to the surface. Its importance extends far beyond its mere physical significance, because the deep water carries nutrients (silicic acid, phosphate and nitrate) and trace metals to the surface where they can be assimilated by phytoplankton. These regions are commercially extremely important and provide almost 90% of the global commercial fish harvest despite comprising less than 3% of the total area of the world's oceans. Upwelling along eastern boundary currents is particularly important as it sustains approximately 11% of the global ocean primary production and 50% of the global fish production (Ryther, 1969). In general, upwelling may be observed along coasts and in open ocean divergence zones (equatorial upwelling).

### 3.2.1 Coastal Upwelling

Upwelling occurs where there is divergent flow at the water surface. Water lost by surface divergence is then replaced by vertical flow. The initial divergent surface flow is induced by specific wind conditions. The most well known upwelling regions are those along certain coasts where wind drives surface water offshore. These regions (Western North America - the California Current region; Northwest Africa - the Canary Current region; and Peru - the Benguela Current region) are typically located along the eastern boundaries of the oceans. Here the dominant winds are part of mid-ocean, semi-stationary, atmospheric high pressure systems (for example the Azores High in the eastern North Atlantic and the North Pacific High).

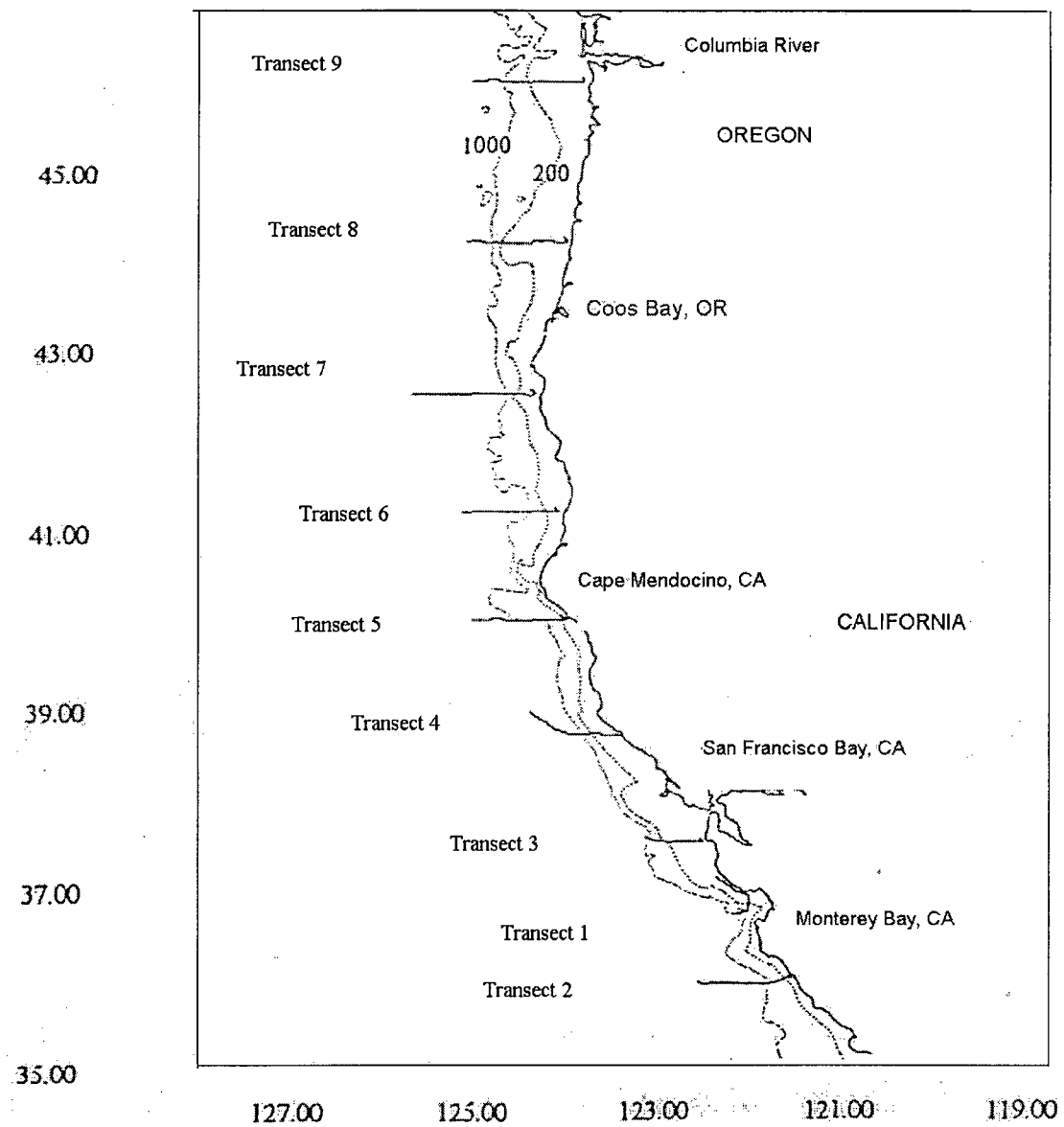
In these regions the predominant wind flow most of the year is nearly parallel to the coastline and toward the equator. Windflow, in conjunction with the influence of the earth's rotation, transports surface water away from the coastline. The earth's rotation gives rise to an apparent force, the Coriolis force, which subjects any moving object to a 'Coriolis Acceleration' directed perpendicular to its motion. In the Northern hemisphere it acts to the right (for an observer looking in the direction of motion); in the Southern hemisphere the Coriolis force acts to the left. The magnitude of the force increases with increasing latitude; it is at a maximum at the North and South Poles and is zero at the equator. When wind blows along the ocean surface it induces both surface waves and currents and energy is transferred by a turbulent process. A force is exerted on the ocean surface in the direction of wind flow - i.e. wind momentum is transferred to the ocean, dragging the surface water along with it. As soon as the water begins to move, it experiences both the Coriolis force and the force of the wind. The resultant effect causes the top most layer of water to be deflected about  $45^\circ$  to the right of the wind direction in the Northern hemisphere and to the left in the Southern. Subsequent deeper layers of water move at angles to the right of the overlying layers. However, frictional losses result in each successive layer moving more slowly than the layer above. The resulting situation is known as an Ekman spiral. In coastal upwelling regimes, such as the California Current region, offshore directed Ekman transport must be replaced by an equal volume of water drawn from depth. The magnitude of Ekman transport directed offshore, determined from the alongshore component of wind stress divided by the

Coriolis parameter, gives an index of the magnitude of coastal upwelling. This is known as the Upwelling Index and is determined by the National Oceanic and Atmospheric Administration (NOAA) for the west coast of America. Higher than average biological productivity and colder than average surface water result from upwelling.

### **3.3 Oceanographic Setting (figure 3.3.1)**

The five eastern boundary current systems (the Canary Current, the Benguela Current, the California Current, the West Australian Current, and the Peru Current) and the strong coastal circulation patterns associated with them are major oceanographic features that influence and determine the physical, chemical and biological makeup of a significant portion of the global ocean. The California Current System extends from Baja California in the south to the Strait of Juan de Fuca in the north. The California Current System is comprised of three primary components; the California Current, the California Undercurrent and the Davidson Current. The California Current is a relatively slow (approximately 10-30cm/sec) and broad (approximately 1000km) equatorward surface flow that extends to about 500m depth. It combines diffuse flow extending many hundreds of kilometers from the coast with localized high velocity zones of southward flow near the coast (Sverdrup *et al*, 1942). It is the primary route for removal of fresh water from the North Pacific and annually carries 20Sv of low salinity, low temperature, high nutrient, high oxygen, cold North Pacific water into the eastern tropical Pacific (Hickey, 1979). The core of the California Current is located approximately 250-350km from the coast at the border of Oregon and California and is about 300km from the coast at Point Conception (Lynn and Simpson, 1987). Both the California Undercurrent and the Davidson Current are poleward flows with the California Undercurrent confined to the continental slope, and the Davidson Current produced as a result of wintertime surfacing of the California Undercurrent off the southern and mid-Californian coast. They typically transport warmer, more saline, low O<sub>2</sub>, high nutrient, equatorial-type water from low to high latitudes.

Coastal upwelling is an important feature of the California Current System with upwelling centers observed off the Washington, Oregon, California and Mexico coasts (see for example Sverdrup *et al*, 1942; Hickey, 1979; Huyer, 1983; Huyer and Kosro,



**Figure 3.3.1**

**Study Area Showing Transcripts Influenced by Upwelling**

1987; Lynn and Simpson, 1987; Rosenfeld *et al*, 1994). Active upwelling appears confined to a narrow coastal band approximately 10-25km wide along the entire coast with water typically upwelled from depths between 30-100m. However, the region influenced by upwelling is much wider, often extending hundreds of kilometers offshore, as eddies, meanders or jets of cold surface waters flow out from coastal headlands such as Cape Blanco. Upwelling is driven by persistent northwesterly winds and adds colder and more saline water to the Southward flowing current. The winds are subject to seasonal cycles and this is reflected in the intensity of the upwelling which reaches a maximum in July/August. The wind pattern over all eastern boundary current systems is ultimately determined by temperature differences between air masses over the land and over the surface layer of the ocean (Crowley and North, 1991). In the case of the Californian Current, strong zonal atmospheric pressure gradients due to greater warming of air masses over western North America relative to the North Pacific are observed during spring and summer. In addition, the pressure gradient varies with position along the coast and with day-to-day variations in the weather. Coastal upwelling occurs year round as far north as San Francisco. South of San Francisco the upwelling is strongest in April, but north of San Francisco the upwelling is strongest in July. Coastal upwelling is relatively weak off central Oregon. Here, short term fluctuations in wind stress with periods of several days are able to cause upwelling despite unfavorable mean monthly wind stress. In July when mean upwelling winds occur along the entire coast, unfavorable wind events seem only to be important in the extreme south (at  $24^{\circ}\text{N}$ ) and in the extreme north (at  $48^{\circ}\text{N}$  and  $51^{\circ}\text{N}$ ). As a consequence of upwelling, one would expect to observe relatively cold water adjacent to the coast wherever the mean monthly Ekman transport is large: northern Baja California in January; from Cape Mendocino to Pt. Conception and along most of Baja California in April; along the entire coast except the Southern California Bight and near the mouth of the Columbia in July; and from Cape Blanco to Pt. Conception and along northern Baja California in September. Often, however, little or no cold water signals are observed off the Columbia River in summertime, and this may be explained by rapid warming of the thin Columbia River plume (Bakun *et al*, 1973).

The time period of this study was coincident with the beginning of an El-Nino

event during which oceanic waters were pushed closer to the shore than in non El-Nino years. The observed trace metal concentrations were found to be consistent with data from previous years and thus the El-Nino event was not considered a significant influence.

### **3.4 Benthic Sources**

#### **3.4.1 Introduction**

Sediments have been identified as a source of dissolved trace metals to overlying waters, and extensive work has been undertaken to explain and quantify the processes leading to the fluxes of dissolved metals from sediments observed in certain areas of the world's ocean (see for example Bruland *et al*, 1978; Bruland and Franks, 1983; Jones and Murray, 1985; Kremling *et al*, 1987, 1989; Kremling, 1985; Muller *et al*, 1994; Le Gall *et al*, 1999). Two major processes have been identified; diagenesis and resuspension.

#### **3.4.2 Diagenesis**

Trace metals are transported to sediments in the form of biogenic detritus, hydrogenous precipitates such as polymetallic oxyhydroxides, and clay minerals. Once buried, they are subject to a variety of physical and chemical process collectively referred to as diagenesis. Physical reactions include alterations in particle size, porosity and mechanical strength; bioturbation by benthic marine organisms which may introduce relatively O<sub>2</sub> rich bottom water into the sediments; and upward advection of pore water following the compaction of sediments allowing the transportation of solutes (Hedges *et al*, 1999; Thramdrup *et al*, 1994). Many of the chemical processes are driven by the oxidation of organic matter which can involve a variety of redox reactions. As a result, suboxic and anoxic conditions are common in sediments and can significantly affect the post depositional behavior of trace metals (see for example Hedges *et al*, 1999; van Geen and Luoma, 1993; Cai and Reimers, 1995). Indeed, trace metals can be remobilized and transported back to the water column through *in-situ* reductive dissolution of FeOOH and MnOOH which contain abundant sorbed metal ions (see for example Heggie *et al*, 1987; Trefrey and Presley, 1982). In open ocean sediments, where the rate of organic matter deposition is slow relative to the re-supply of O<sub>2</sub> by thermohaline circulation, the top 8-

20cm will be oxic. Below this, benthic respiration is sufficiently fast to maintain suboxic and anoxic conditions. In the coastal ocean, the deposition rate is fast enough to cause the redox boundary to migrate to within 5cm of the sediment interface, and in upwelling areas, subject to high organic matter fluxes, the anoxic zone extends into the bottom waters. Below the oxic/anoxic boundary, Fe and Mn oxyhydroxides are utilized as oxidizing agents and are themselves reduced to  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  which are then free to diffuse upwards. In the open ocean, the redox boundary is usually deep enough to severely limit the amount of dissolved  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  that can diffuse out of the sediments, instead they are rapidly re-oxidised and re-precipitated as oxyhydroxides upon contact with  $\text{O}_2$ . In coastal environments, however, the redox boundary is sufficiently close to the sediment-water interface to allow significant quantities of dissolved metals to escape to bottom waters (Hedges *et al*, 1999; Carpenter *et al*, 1982).

#### 3.4.3 Sediment resuspension

Sediments may be resuspended through bottom water turbulence or current shear. This primarily affects fine grained sediments some of which may be small enough to pass through  $0.45\mu\text{m}$  filters, therefore leading to elevated total dissolvable trace metal concentrations. Resuspension may also introduce small quantities of pore water into the overlying water column. In addition, resuspension may increase the 'truly' dissolved fraction through a reversible exchange mechanism (Moran and Moore, 1988; Balls, 1989; Kremling and Hydes, 1988; Van Beusekom, 1988). These authors have suggested a mechanism involving adsorptive-exchange between solution and sediment phases where the exchange process may be described in terms of a distribution coefficient,  $K_d$ .

The equation defining  $K_d$  is:

$$K_d = C_s / (C_d \times S)$$

Where  $C_s$  is the concentration of the adsorbed metal,  $C_d$  is the concentration of dissolved metal and  $S$  is the concentration of suspended sediment.

For suspended sediment concentrations around 10mg/l, adsorptive-exchange between sediment and solution phases may have a significant impact on the solution phase concentration of metals.

### **3.5 Prior trace metal studies**

#### **3.5.1 Upwelling**

Several studies have been undertaken on the effect of coastal upwelling on trace metal (and nutrient) concentrations (see for example Bruland and Franks (1983); Kremling (1985); Kremling and Hydes (1988); Kremling and Pohl (1989); Muller *et al* (1994); Le Gall *et al* (1999); El Sayed *et al* (1994); Loscher *et al* (1999)). With reference to the metals studied in this research, examples of prior work citing upwelling as a cause of concentration elevation include high Cd concentrations observed in Pacific coastal surface waters near the California-Mexico border ( $\sim 0.20\text{nM}$ , Segovia-Zavala *et al*, 1998; Sanudo-Wilhelmy and Flegal, 1991), off central and northern California ( $0.6\text{nmol/kg}$ , van Geen and Husby, 1996) off Baja California ( $0.26\text{nM}$ , Sanudo-Wilhelmy and Flegal, 1996), and at the mouth of the San Francisco estuary ( $0.96\text{nmol/kg}$ , Flegal *et al*, 1991) where background Cd signals for all works cited were  $\sim 0.06\text{-}0.15\text{nM}$ ; elevated Cu and Mn concentrations (upwelled Cu  $3.4\text{nmol/l}$ , background Cu  $2.1\text{nmol/kg}$ ; upwelled Mn  $19.3\text{nmol/l}$ , background Mn  $4.2\text{nmol/kg}$ ) observed in surface waters off the Gulf of Lions in the Mediterranean Sea (Elsayed *et al*, 1994); enhanced Cu signals in upwelled waters of the Namibian shelf (Rutgers van der Loeff, 1996); and elevated Mn concentrations observed over the northeast Pacific continental slope (Jones and Murray, 1985) and at the California-Mexico border (Sanudo-Wilhelmy and Flegal, 1991) (upwelled Mn  $16\text{nmol/kg}$ ; background Mn  $\sim 5\text{-}7\text{nmol/kg}$ ).

#### **3.5.2 Sediment sources**

Coastal sediments have been identified as a source of dissolved Mn, Cd, Cu and Al to overlying waters, though the degree of enrichment and the route by which it occurs varies depending on the metal and the region.

Fluxes of dissolved Mn from reducing shelf sediments have been observed in many coastal regions including northwest European shelf waters (Kremling, 1985; Le



Gall *et al*, 1999), waters off the Washington (Jones and Murray, 1985) and California coasts (Landing and Bruland, 1980, 1987), and shelf waters of the Bering Sea (Minakawa, 1998).

Elevated levels of dissolved Al observed in deep relative to intermediate waters of the Arctic (Moore, 1981) and North Atlantic (Measures *et al*, 1986; Hydes, 1979; Measures *et al*, 1984; Hall and Measures, 1997) potentially point to resuspended sediments as a source of dissolved Al to overlying waters. In particular it has been suggested that resuspension of surface sediments in high energy western boundary currents may provide a mechanism for supplying dissolved Al to deep waters in certain regions (Measures *et al*, 1984; Moran and Moore, 1988). However, in the Guinea/Angola basin of the South Atlantic (Measures and Edmund, 1990) where dust inputs to surface waters are significant and circulation is slow in deep waters, little if any significant flux of dissolved Al into bottom waters was observed. Similarly, in the Pacific Ocean (Orlans and Bruland, 1986, 1988), the distribution of Al in deep waters indicates only minimal enrichment of Al from sedimentary sources. And authors such as Measures and Edmond (1990) are suggesting enrichment in deep eastern Atlantic waters is due, primarily, to advective features. Further work investigating and quantifying the diagenic behavior of Al in pore waters needs to be performed before a definitive answer to the source of Al in deep waters can be obtained.

Sediment fluxes have been proposed as sources of Cu by many authors including Heggie *et al* (1987) in waters overlying the Bering Sea continental shelf, Croot *et al* (1998) for shelf waters of the Otago Peninsula, New Zealand, Flegal *et al* (1991) in the San Francisco Bay, Bruland *et al* (1980) from the North Pacific, Sanudo-Wilhelmy and Flegal (1996) in waters off Baja California, Heggie *et al* (1982) from the central Bering Sea, Kremling (1983) from waters around the British Isles, Jickells and Burton (1987) from the Sargasso Sea, Saager *et al* (1997) from the northeast Atlantic, and Saager *et al* (1992) from the Arabian Sea Basin.

### 3.6 Results

#### 3.6.1 Background

Over 400 samples were collected off the west coast of North America during June and July 1997. Note that all trace metals referred to in this section are termed dissolved. A constituent is defined as being dissolved when it passes through a  $0.45\mu\text{m}$  filter. This filter size is an operationally determined parameter. The assumption that  $0.45\mu\text{m}$  is a suitable cut-off for particulate species will not be justified in all cases. For example, colloidal material formed in scavenging processes can pass through a filter of this size, and thus would be mistakenly 'counted' as truly dissolved material. Background California Current surface water values were determined for Mn (3-5nmol/kg), Al (0.38-0.65nmol/kg), Cd (0.08-0.30nmol/kg) and Cu (0.79-2.2nmol/kg). These values reflect water that is not impacted by local upwelling or riverine processes. These data agree well with previous work. Mn values agree with Landing and Bruland (1980) who reported values ranging from ~4-6nM in California Current waters off Santa Cruz and Jones and Murray (1985) who reported values ranging from ~4-8nM in waters off Washington. The Al data agree with Orians and Bruland (1986) who determined Al values ranging from 0.3-1nmol/kg in California Current waters off Santa Cruz. Cd values agree with Bruland (1980) who reported values of 0.06-0.16nmol/kg for waters off Santa Cruz. Cu values agree with numerous authors including Bruland (1980) who reported values up to 1.2nmol/kg in the California Current off Santa Cruz, Boyle *et al* (1977) who observed values of approximately 1.1-1.4nmol/kg in the California Current and Sanudo-Wilhelmy *et al* (1996) who observed values around 0.9-1.9nmol/kg in coastal waters off Baja California.

#### 3.6.2 Physical data, nutrients and Chl. a

Temperature, salinity, nutrient and Chl. a data indicate that transects WCSST01-06 and WCSST08 are strongly influenced by upwelling. Location, salinity, temperature, nutrient, Chl. a and trace metal data are recorded in full in appendix 1.

Figures 3.6.2.1-3.6.2.2 show sea surface temperature satellite images of California Current waters during the time period of this cruise. Figure 3.6.2.1 shows data averaged over the time period June 15, 1997–June 30, 1997. Figure 3.6.2.2 shows data averaged

over the time period July 01, 1997–July 15, 1997. The data were obtained from the NOAA/NESDIS Coastwatch program. Data from June show upwelling occurring between about 42°N (just north of Cape Mendocino) and about 37°N (just south of San Francisco Bay). Waters in this area are cold ( $<14^{\circ}\text{C}$ ), and a patch of very cold water is observed just off Cape Mendocino ( $<13^{\circ}\text{C}$ ). NOAA/NESDIS reported above average north-northeasterly winds during this month producing a modestly high value for the upwelling index. Data from July show upwelling occurring in the same area as in June, but waters are now slightly warmer and the patch of intense upwelling off Cape Mendocino appears to have decreased in size. NOAA/NESDIS reported persistent northwesterly winds and normal upwelling during this month. It is important to realize that upwelling may initially occur very close to the coast; upwelled waters may then be rapidly transported or advected offshore to locations which were then sampled.

Temperature, salinity and nutrient (figures 3.6.2.3-3.6.2.8) maps reflect the position and extent of several water mass features typically seen in this region during summertime and are also indicative of the typical circulation. Note that nutrient and Chl. a data are plotted with respect to either temperature or salinity, depending on which of these properties give the clearest indication of upwelled waters. Recently upwelled water is identified by low temperature ( $t=8.5\text{--}11.6^{\circ}\text{C}$ ), high salinity ( $s=32.5\text{--}33.5$ ) and elevated nutrient (nitrate= $13\text{--}33\mu\text{M}$ ; silicate= $15\text{--}45\mu\text{M}$ ) signals. These data agree well with upwelling studies previously undertaken in this area. Rosenfeld *et al* (1993) identified upwelling as the source of cold ( $t<10.5^{\circ}\text{C}$ ), salty ( $s>33.7$ ) near-surface water frequently seen in the San Francisco Bay area in spring-summer 1993. Service *et al* (1998) observed a continuous band of cold water ( $t<10.1^{\circ}\text{C}$ ) next to the Monterey Bay coastline following several days of northwesterly winds during springtime. Huyer (1983) identified upwelling as the source of cold ( $t=12^{\circ}\text{C}$ ), salty ( $s>33$ ) water observed off the coasts of California, Oregon and Washington in the summers of 1950, 1963, 1968 and 1970.

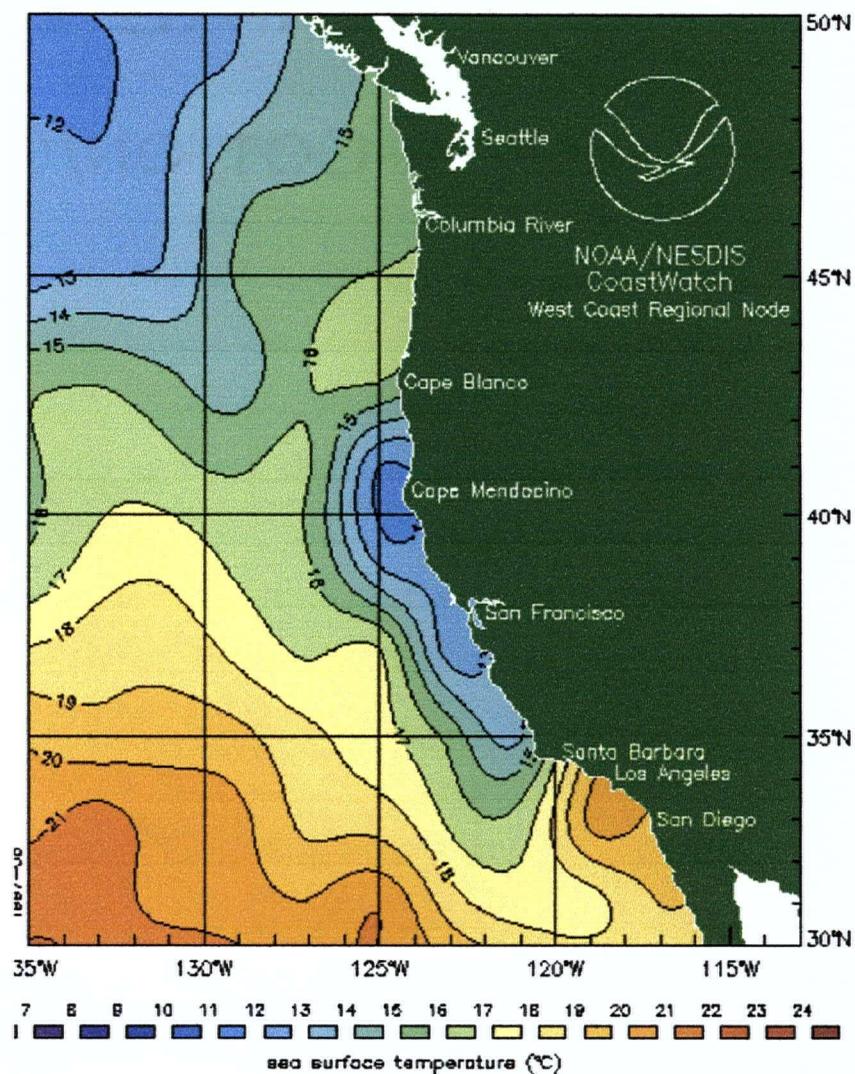


Figure 3.6.2.1

Sea surface temperatures for California Current waters. Data is averaged over the time period June 15-June 30, 1997. Data is obtained from NOAA/NESDIS Coastwatch Program.



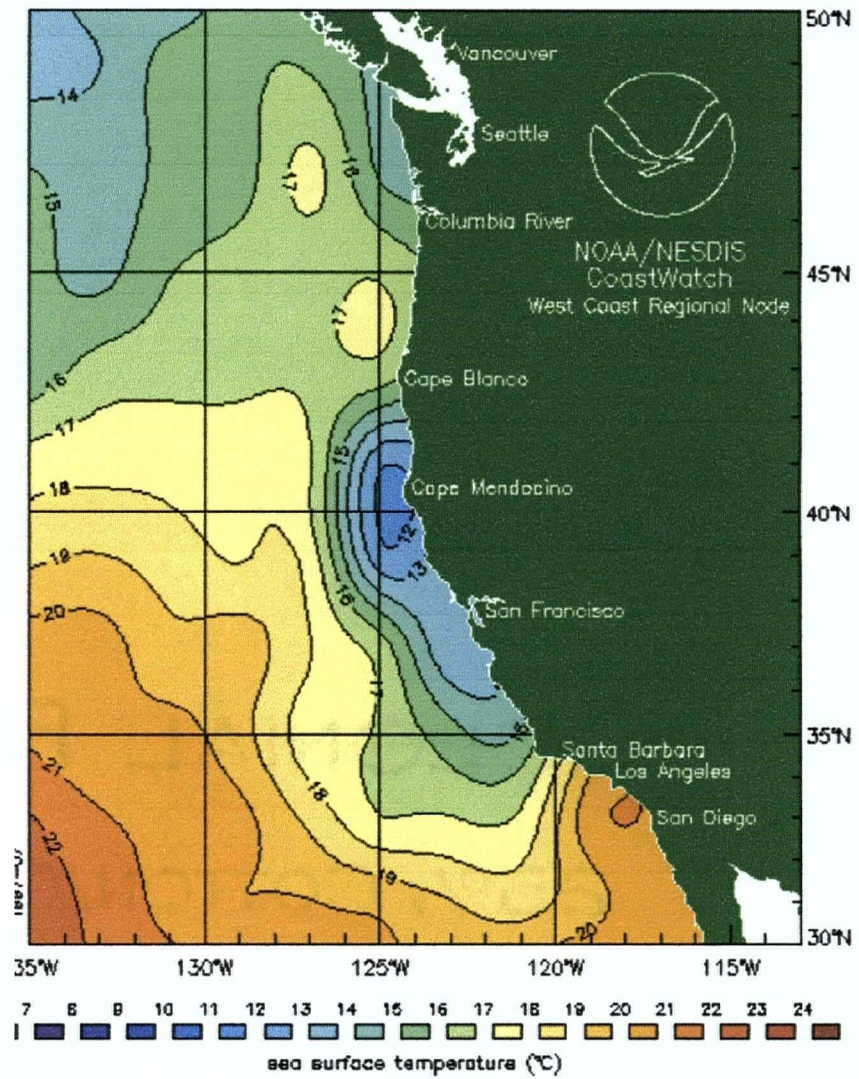


Figure 3.6.2.2

Sea surface temperatures for California Current waters. Data is averaged over the time period July 1 – July 15, 1997. Data is obtained from NOAA/NESDIS Coastwatch Program.

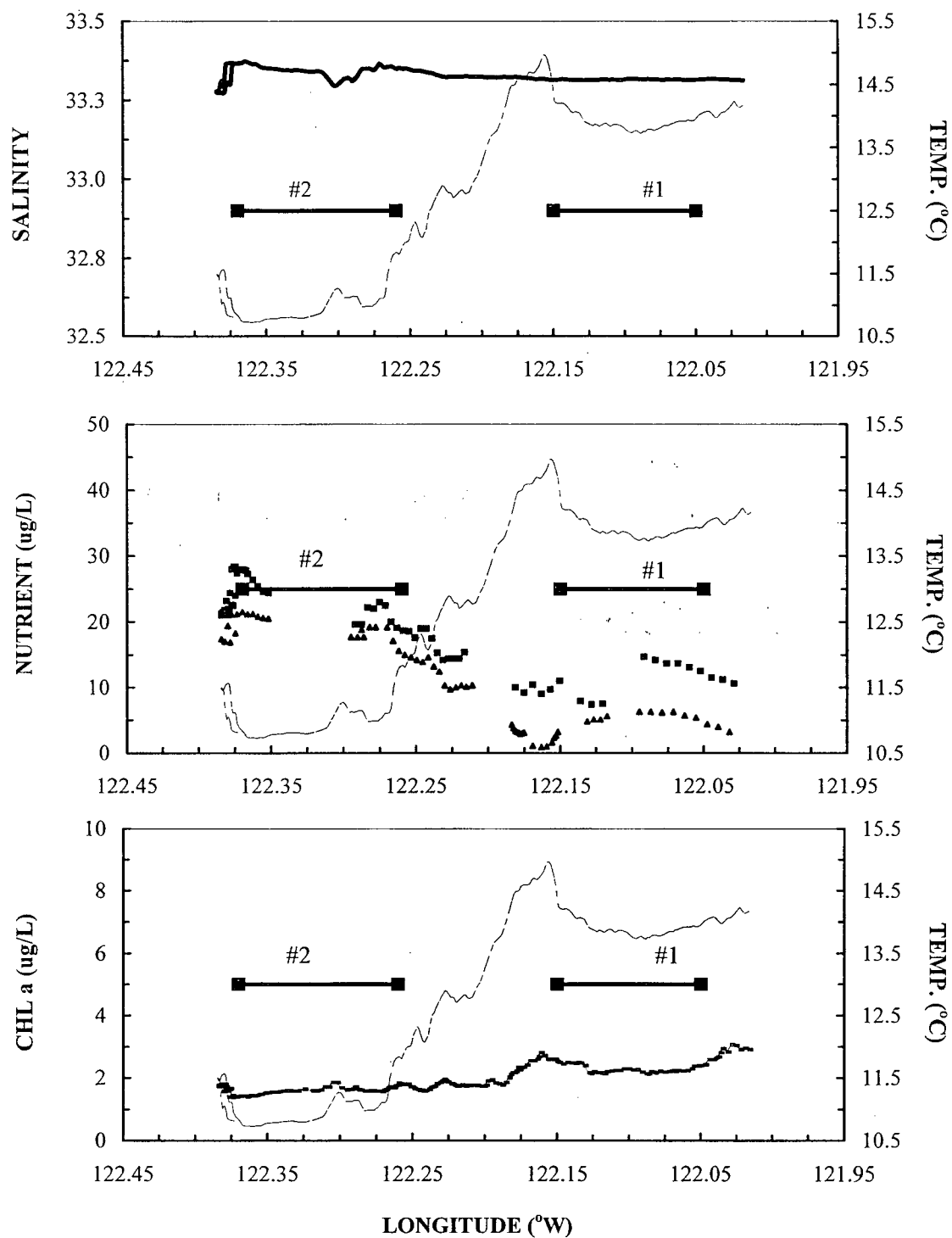
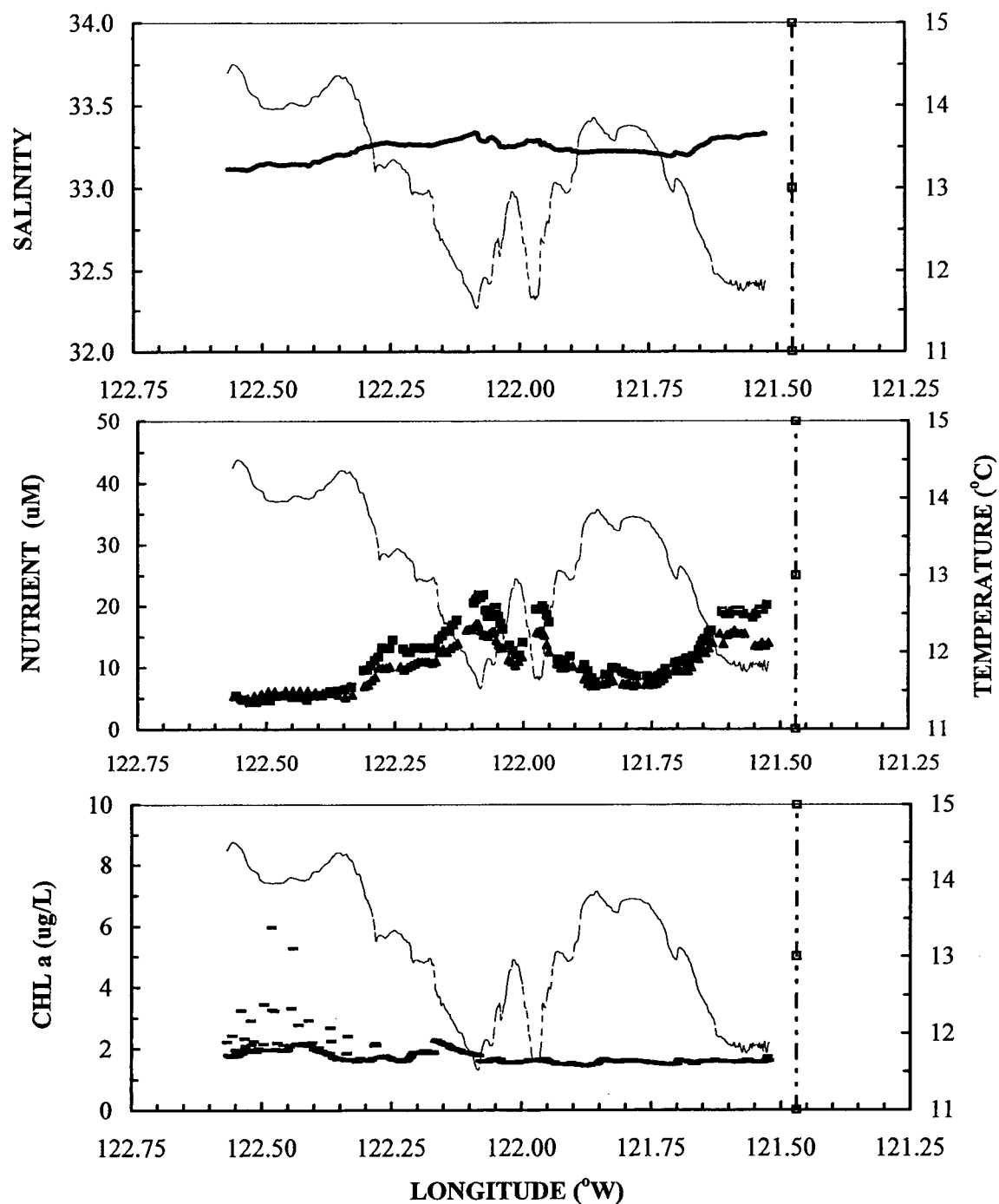


Figure 3.6.2.3

Temperature, salinity, nutrients and chlorophyll a data for WCSST 01

(Legend: solid line = salinity; broken line = temperature; ■ = silicate; ▲ = nitrate;

— = Chl a; upwelling regimes are denoted by bold lines and numbers)



**Figure 3.6.2.4** Temperature, salinity, nutrients and chlorophyll a data for WCSST 02  
 (Legend: solid line = salinity; broken line = temperature; vertical line = coastline;  
 ■ = nitrate; ● = silicate; — = Chl a )

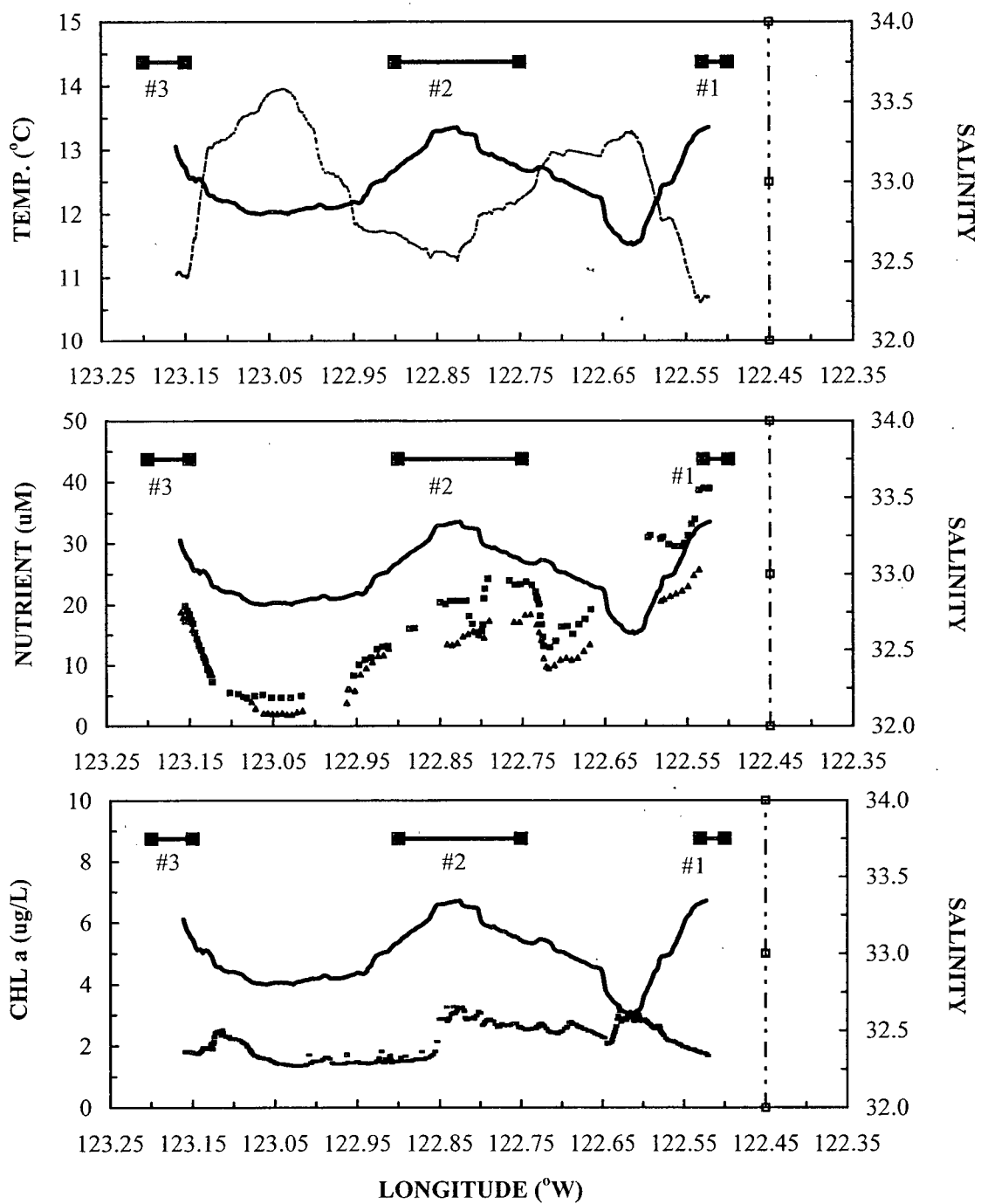
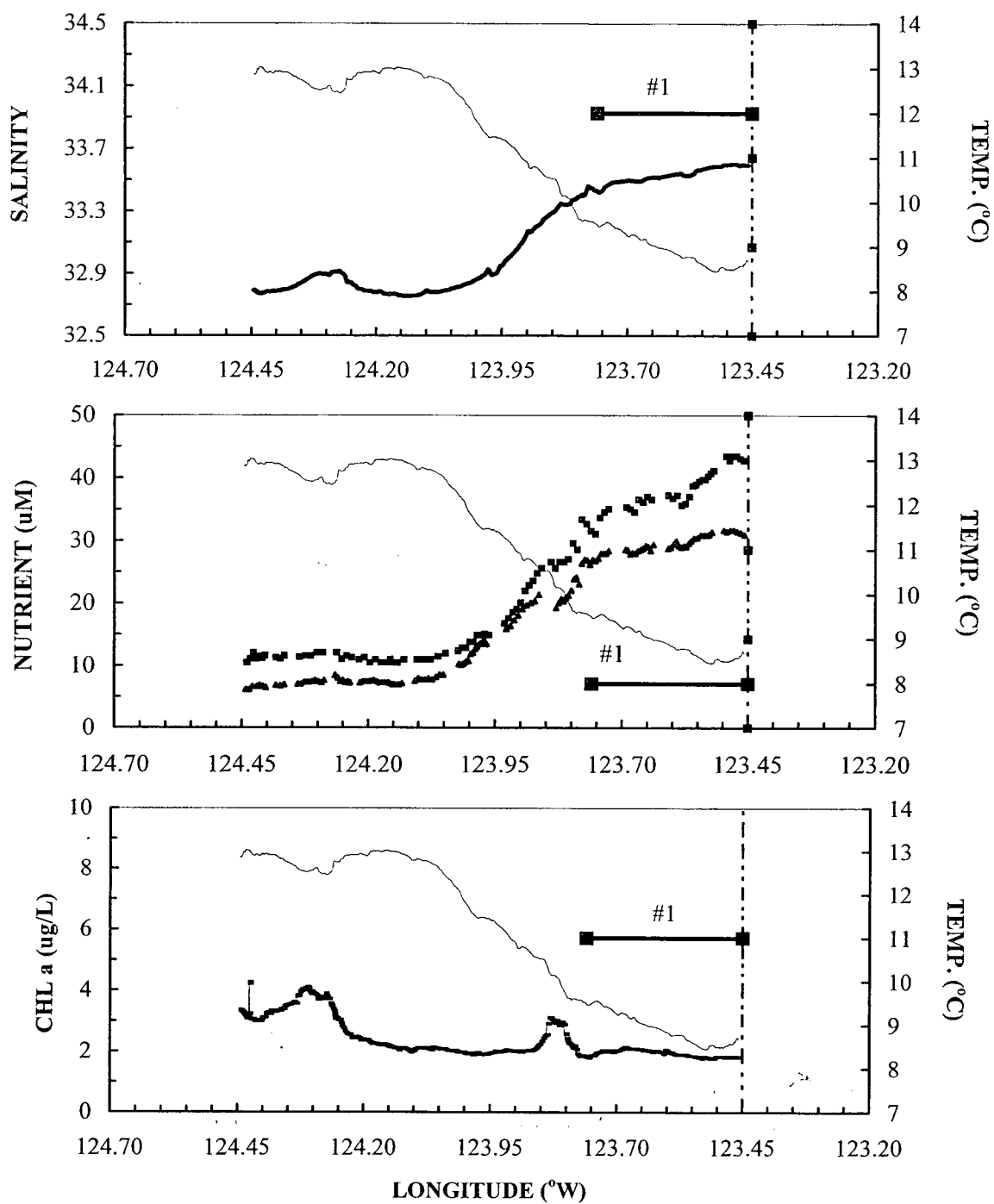


Figure 3.6.2.5

Temperature, salinity, nutrients and chlorophyll a data for WCSST 03

(Legend: solid line = salinity; broken line = temperature; vertical line = coastline;  
 ■ = silicate; ▲ = nitrate; — = Chl a; # = upwelling regimes)





**Figure 3.6.2.6**  
**Temperature, salinity, nutrients and chlorophyll a data for WCSST 04**

(Legend: solid line = salinity; broken line = temperature; vertical line = coastline;  
 ■ = silicate; ▲ = nitrate; — = Chl a; # = upwelling regime )

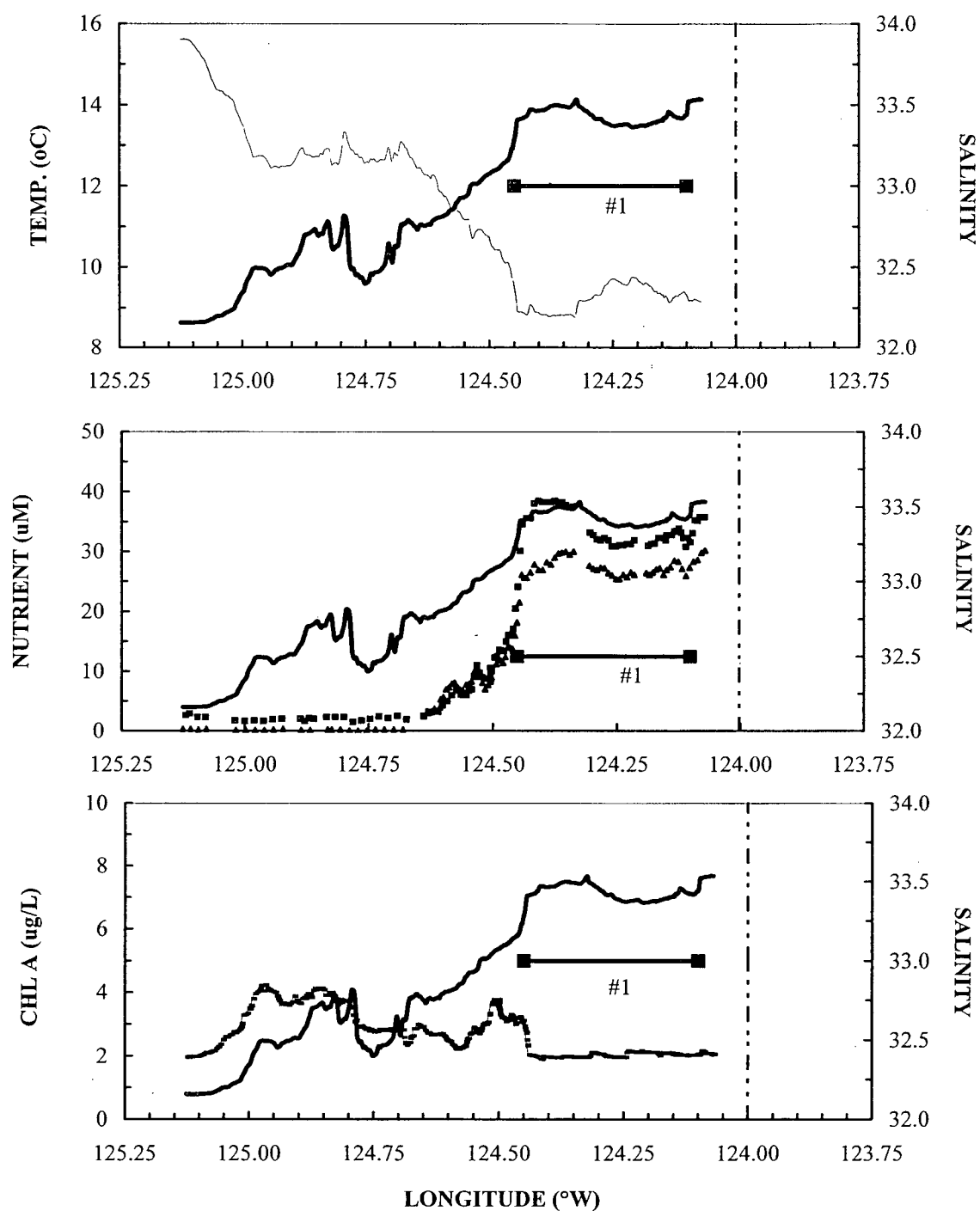


Figure 3.6.2.7

Temperature, salinity, nutrients and chlorophyll a data for WCSST 05

(Legend: solid line = salinity; broken line = temperature; vertical line = coastline;  
 ■ = silicate; ▲ = nitrate; — = Chl a; # = upwelling regime)

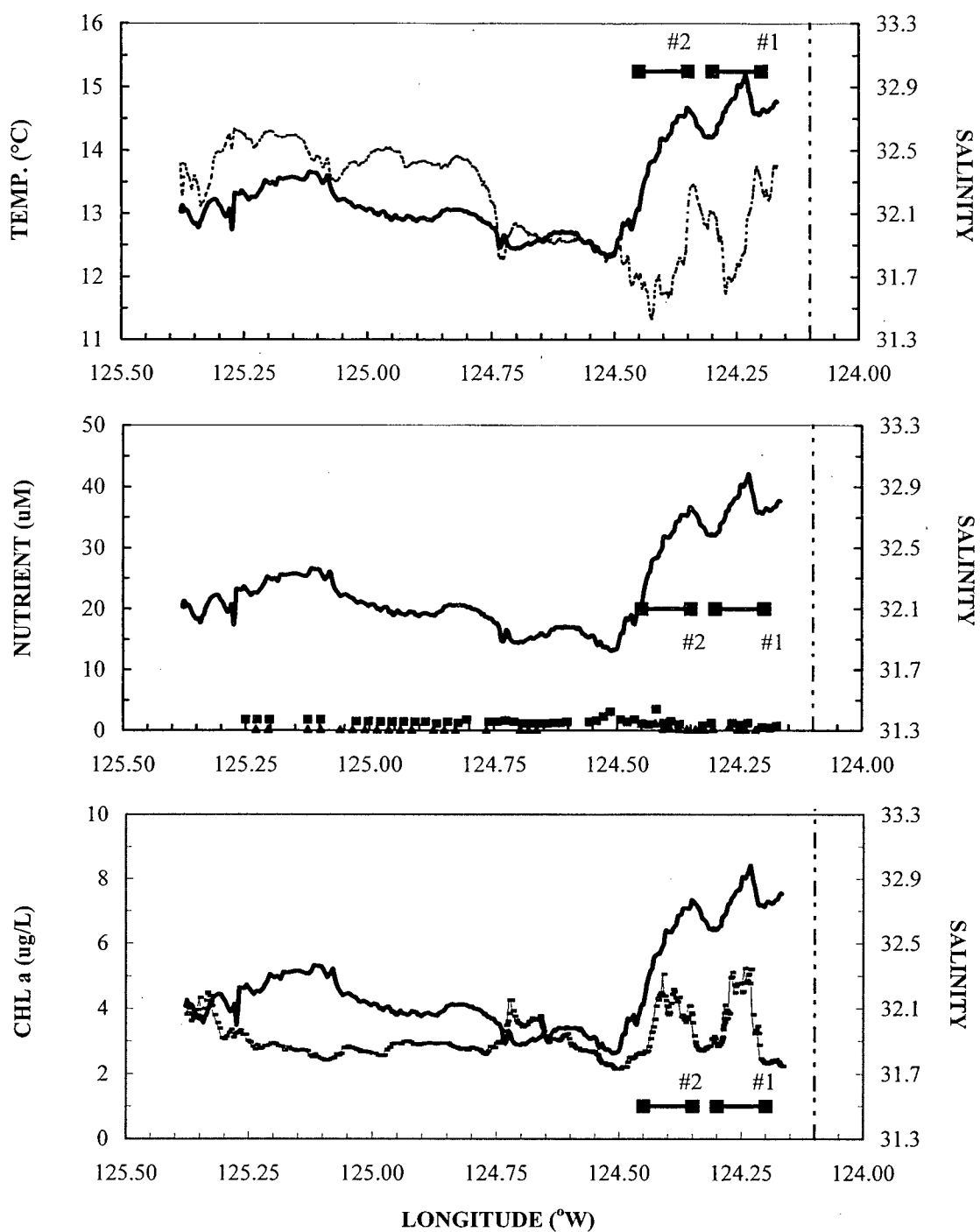


Figure 3.6.2.8

Temperature, salinity, nutrients and chlorophyll a data for WCSST 06

(Legend: solid line = salinity; broken line = temperature; vertical line = coastline;  
 ■ = silicate; ▲ = nitrate; — = Chl a; # = upwelling regime)

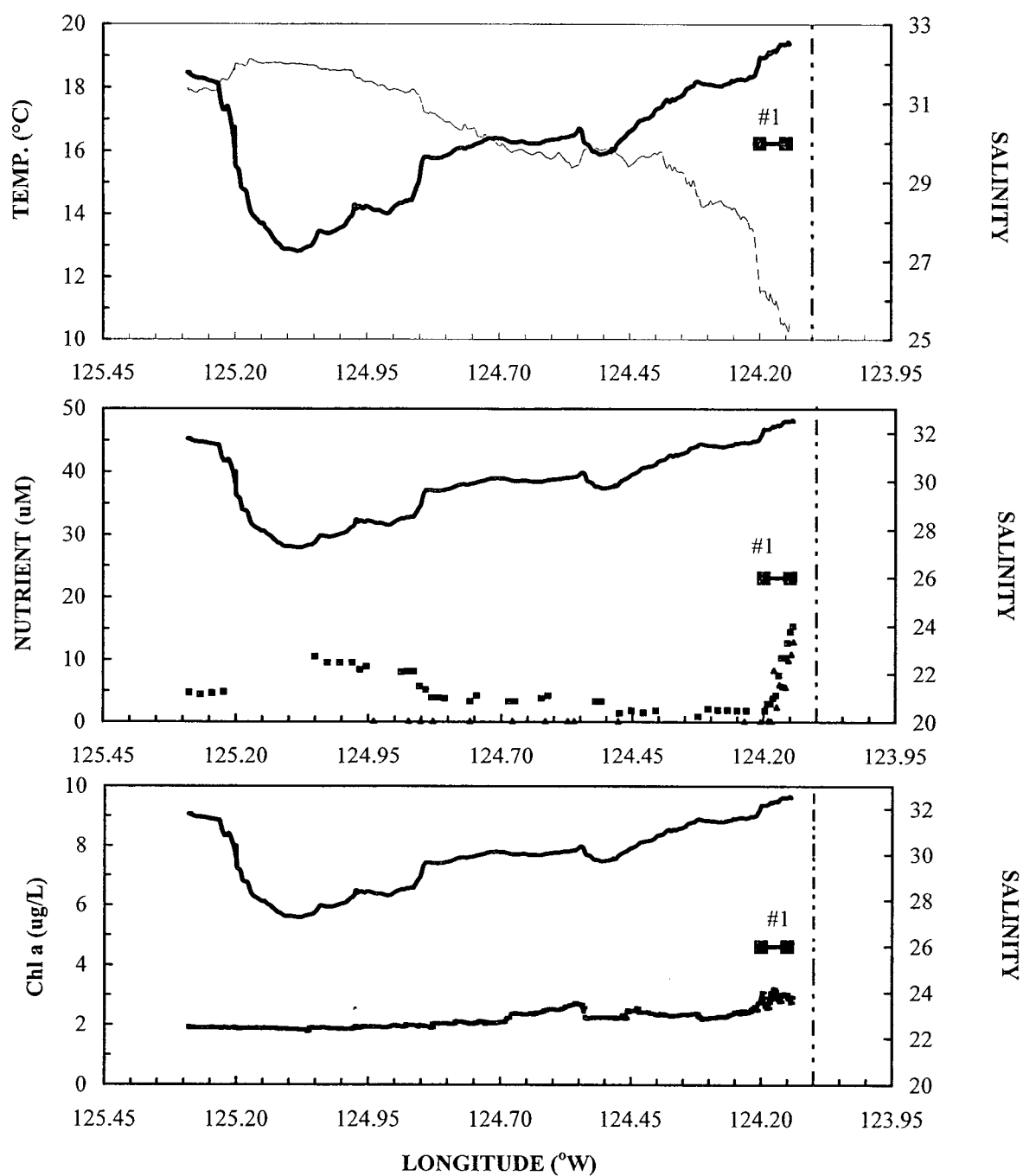


Figure 3.6.2.9

Temperature, salinity, nutrients and chlorophyll a data for WCSST 08

(Legend: solid line = salinity; broken line = temperature; vertical line = coastline;  
 ■ = silicate; ▲ = nitrate; — = Chl a; # = upwelling regime)

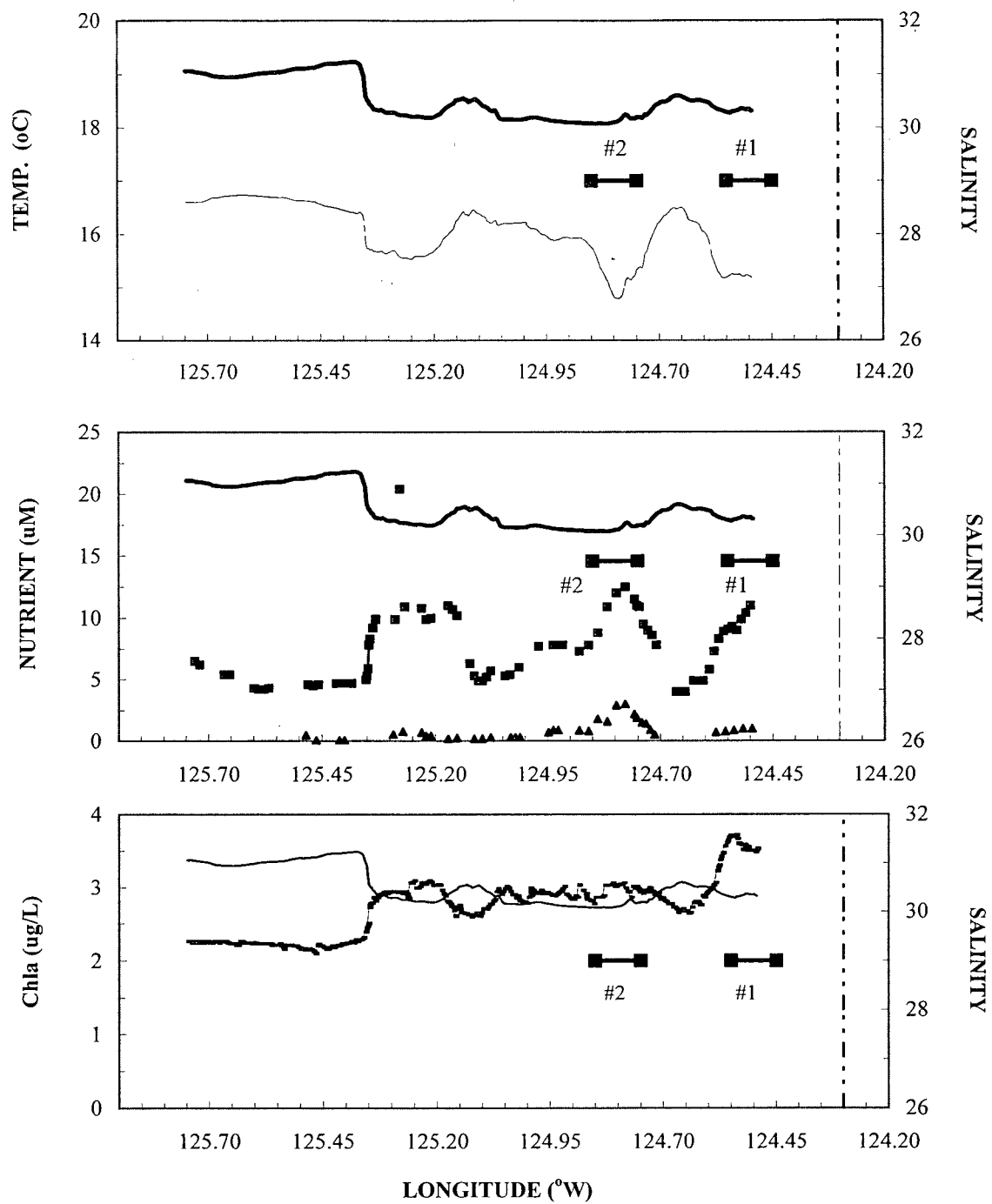


Figure 3.6.2.10

Temperature, salinity, nutrients and chlorophyll a data for WCSST 10

(Legend: solid line = salinity; broken line = temperature; vertical line = coastline;  
 ■ = silicate; ▲ = nitrate; — = Chl a; # = upwelling regime )

### 3.6.3 Trace metal data (figures 3.6.3.1-3.6.3.10; table 3.6.3.1)

Dissolved Mn, Al, Cd and Cu concentrations are summarized in appendix 1. Transect plots showing trace metal data along with temperature or salinity data versus longitude are shown in figures 3.6.3.1-3.6.3.7. Concentration data are plotted versus salinity or temperature depending on which variable best illustrates upwelling. "Dog legs", where the ship initially traveled inshore, are differentiated from the outbound leg of the transect on the maps, and data relating to these "dog-legs" are also recorded in full in appendix 1. Table 3.6.3.1 shows the ranges of trace metal concentrations within the upwelling regimes of transects WCSST01-WCSST06, WCSST08 and WCSST10. Reference will also be made to iron (Fe) and cadmium (Cd) data provided by the Bruland laboratory at the Institute of Marine Sciences, University of California, Santa Cruz and gallium (Ga) data provided by Lanthier (1999).

### 3.6.4 WCSST01

WCSST01 data are plotted for the section from Ano Nuevo to Santa Cruz. Data from Santa Cruz to Monterey Bay (2 stations only) and the subsequent dog-leg are recorded only in the appendix.

Salinity is relatively constant and high throughout the entire transect. Sea surface temperature and nutrient data suggest one recent upwelling regime (#2: 122.26-122.36°W). The high salinity/high temperature signal observed in the southeastern section of the transect is likely to be from older, advected upwelled water from Ano Nuevo just to the north of Monterey Bay which has been depleted of its nutrients and warmed (regime #1: 122.05-122.15).

Mn, Cu and Cd show elevation coincident with region #2 – the newer upwelling regime. All three metals are at background at the older regime (#1). Al remains constant and at background across the entire transect.

**Table 3.6.3.1 Trace metal data for Mn, Al, Cd and Cu (WCSST01-WCSST06, WCSST08, WCSST10)**

| Transect | Upwelling Location (°W) | Salinity | Temp. (°C) | Silicic acid/nitrate (umol/kg) | Mn        | Cd        | Al (nmol/kg) | Cu        | Ga    |
|----------|-------------------------|----------|------------|--------------------------------|-----------|-----------|--------------|-----------|-------|
| WCSST01  | #1 122.05-122.15        | 33.3     | 13-13.5    | 20-30/18-20                    | 6.9-9.2   | 0.14-0.28 | 0.48-0.55    | 0.71-1.20 | n/a   |
|          | #2 122.26-122.36        | 33.3     | 10.7-11.2  | 11-15/4-5                      | 12.0-17.6 | 0.57-0.74 | 0.47-0.53    | 2.39-2.67 | n/a   |
| WCSST02  | #1 121.50-121.65        | 33.3     | 11.75      | 20-21/16                       | 4.2-6.2   | 0.44-0.48 | 0.49-0.54    | 1.66-2.27 | 7-8   |
|          | #2 121.95-121.99        | 33.3     | 11.60      | 21/16                          | 3.4       | 0.47-0.48 | 0.50-0.52    | 1.17-1.25 | 6     |
|          | #3 122.05-122.15        | 33.3     | 11.50      | 22/16                          | 2.6-2.9   | 0.43-0.44 | 0.49-0.52    | 0.94-0.96 | n/a   |
| WCSST03  | #1 122.53               | 33.4     | 10.60      | 30-40/20-26                    | 33-36.7   | 0.84-0.92 | 0.69-0.74    | 3.89-4.52 | 11    |
|          | #2 122.75-122.90        | 33.3     | 11.30      | 20-25/12-16                    | 10.2-25.1 | 0.54-0.76 | 0.65-0.72    | 2.57-3.54 | 8     |
|          | #3 123.15-123.20        | 33.6     | 11.00      | 20/19                          | 3.8-4.5   | 0.14-0.27 | 0.54-0.58    | 1.80-2.32 | 7     |
| WCSST04  | #1 123.45-123.80        | 33.5     | 8.50       | 25-41/20-30                    | 8.0-13    | 0.55-0.93 | 0.57-0.67    | 1.91-3.79 | 10-11 |

n/a indicates data are not available

Table 3.6.3.1 continued

| Transect | Upwelling Location (°W) | Salinity  | Temp. (°C) | Silicic acid/nitrate (umol/kg) | Mn       | Cd        | Al (nmol/kg) | Cu        | Ga     |
|----------|-------------------------|-----------|------------|--------------------------------|----------|-----------|--------------|-----------|--------|
| WCSST05  | #1 124.1-124.45         | 33.3-33.5 | 8.8-9.2    | 30-35/25-28                    | 6.8-25.2 | 0.69-0.83 | 0.55-0.66    | 1.93-4.33 | 7.5-13 |
| WCSST06  | #1 124.2-124.3          | 32.9-33.0 | 11.6-12.0  | 1-2/0-1                        | 6.5-7.9  | 0.36-0.40 | 0.50-0.54    | 2.03-2.61 | 7      |
|          | #2 124.35-124.45        | 32.7      | 11.2       | 1-2/0-1                        | 6.4-6.9  | 0.30-0.35 | 0.52-0.56    | 1.99-2.12 | 4-5    |
| WCSST08  | #1 124.15-124.20        | 32-32.5   | 10.4-10.5  | 14-15/10                       | 14.1     | 0.45-0.48 | 0.61-0.63    | n/a       | n/a    |
| WCSST10  | #1 124.45-124.55        | 30.3      | 15.0       | 10-11/0.9-1                    | 6.3-6.4  | 0.22-0.26 | 0.52-0.56    | 0.91-0.98 | n/a    |
|          | #2 124.75-124.85        | 30.5      | 14.4       | 10-12/2-3                      | 5.7-6.6  | 0.27-0.38 | 0.47-0.54    | 1.60-2.90 | n/a    |

n/a indicates data are not available

Background values: Mn (3-5nmol/kg), Al (0.38-0.65nmol/kg), Cd (0.08-0.30nmol/kg) and Cu (0.70-2.20nmol/kg)



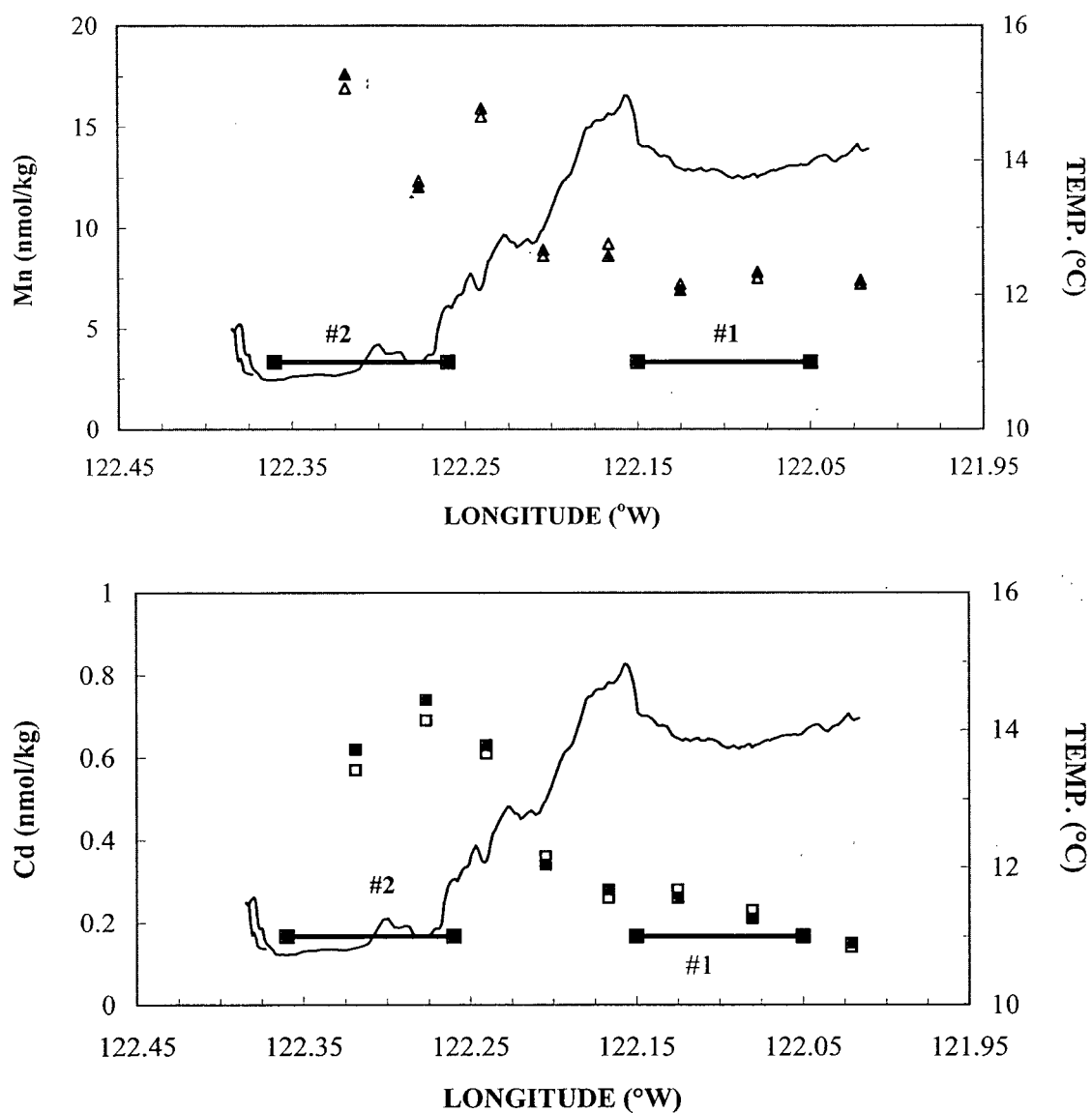


Figure 3.6.3.1

Trace metal data for WCSST 01.

(Legend: solid line = salinity; open/closed  $\blacktriangle$  = Mn replicates; open/closed  $\blacksquare$  = Cd replicates; vertical broken line = coastline; # = upwelling regimes)

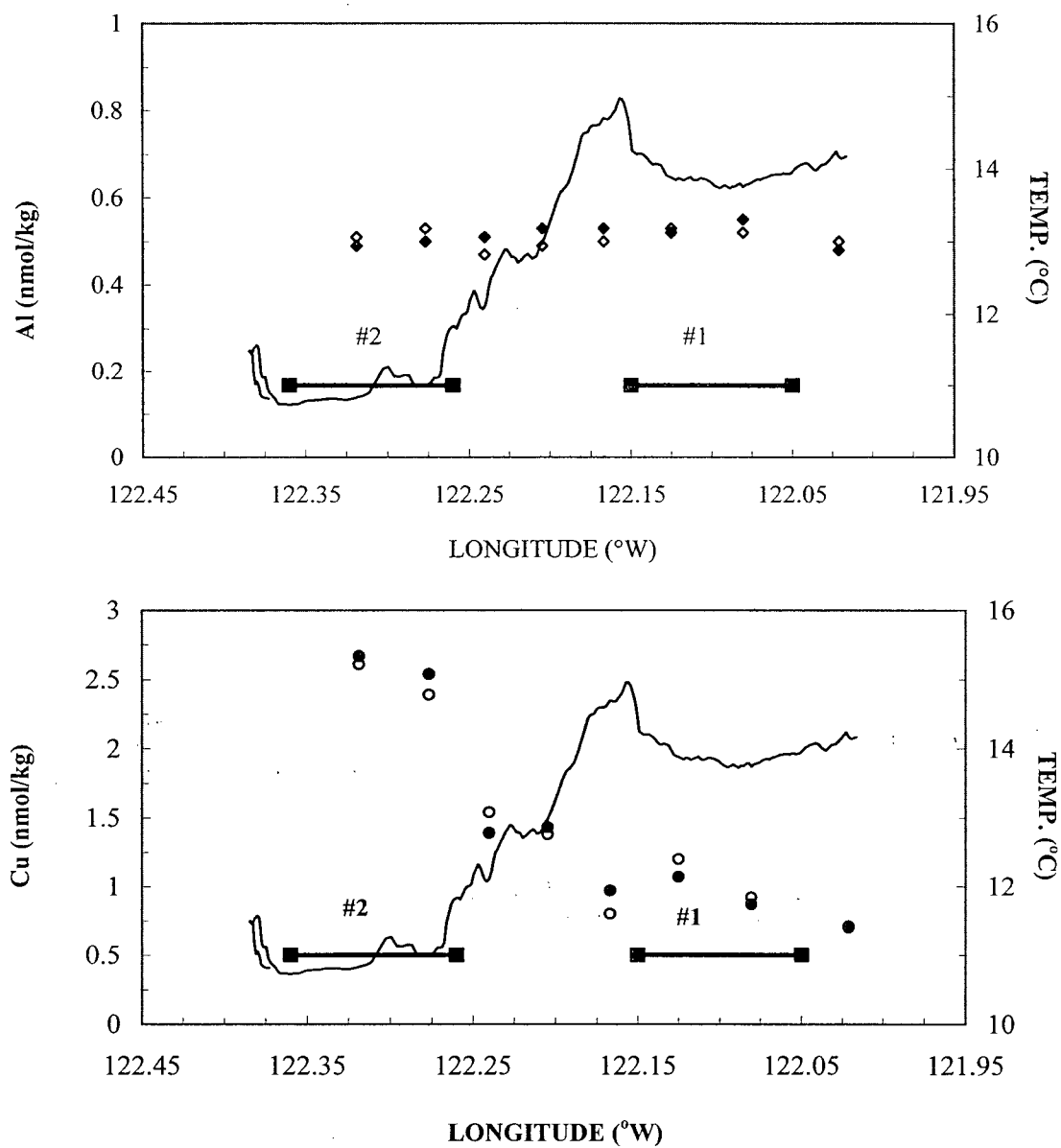


Figure 3.6.3.1

Trace metal data for WCSST 01.

(Legend: solid line = salinity; open/closed  $\diamond$  = Al; open/closed  $\bullet$  = Cu; vertical broken line = coastline; # = upwelling regimes)

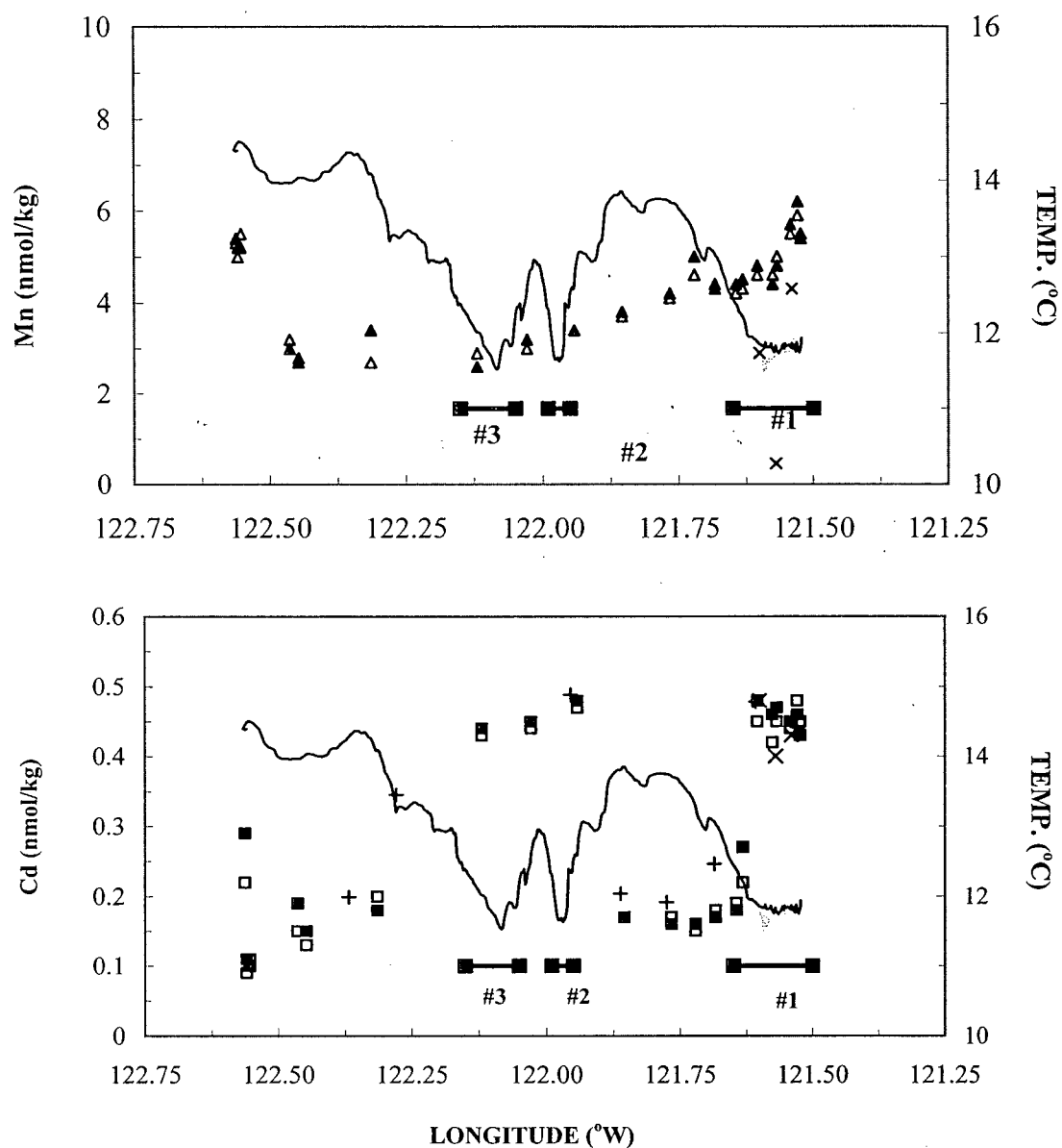


Figure 3.6.3.2

Trace metal data for WCSST 02.

(Legend: solid line = salinity; open/closed  $\blacktriangle$  = Mn replicates; open/closed  $\blacksquare$  = Cd replicates; + = Cd UCSC data; # = upwelling regime; X = 'dog-leg' data)

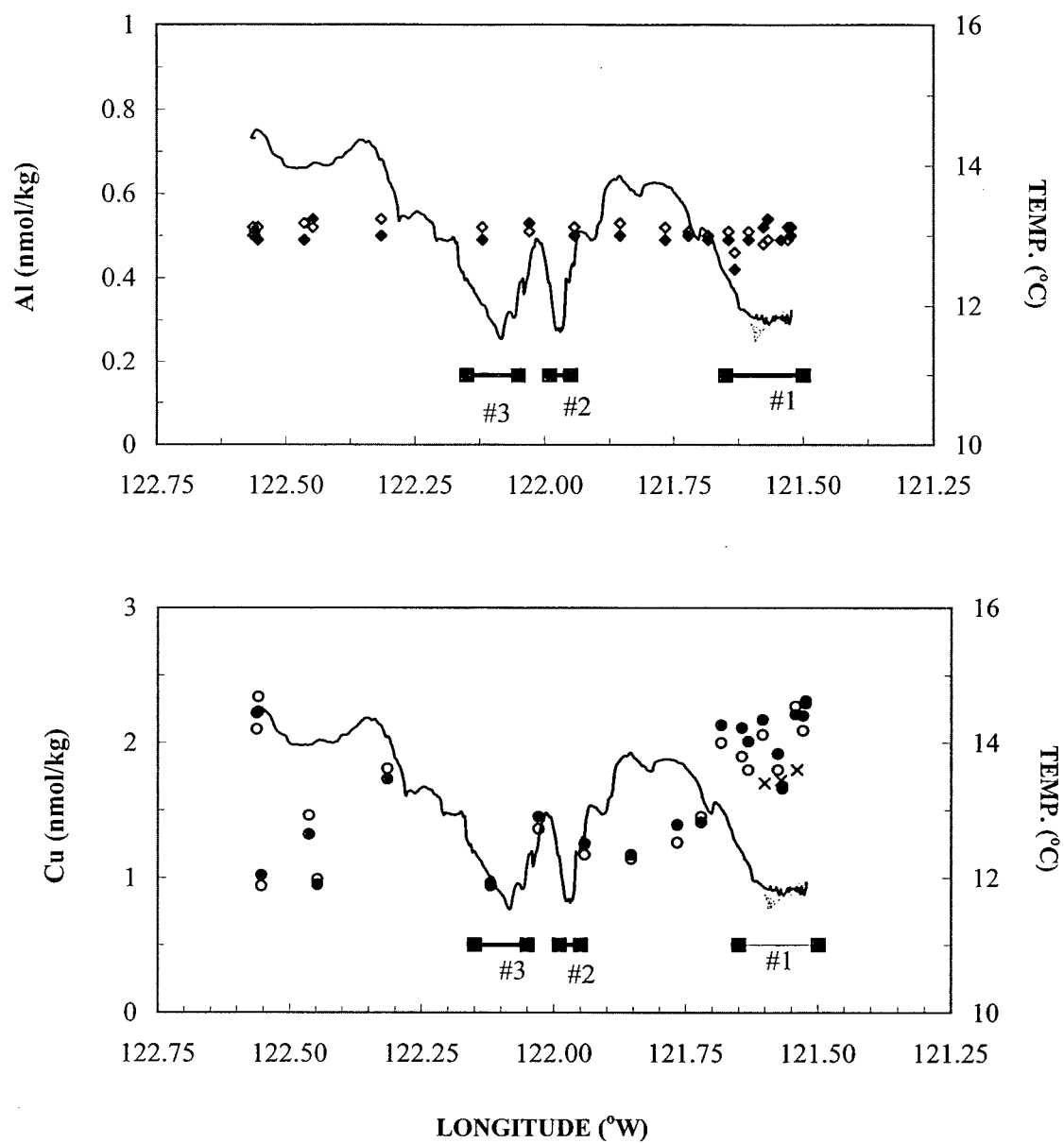


Figure 3.6.3.2

Trace metal data for WCSST 02.

(Legend: solid line = salinity; open/closed  $\diamond$  = Al replicates; open/closed  $\bullet$  = Cu replicates; # = upwelling regime; X = 'dog-leg' data)

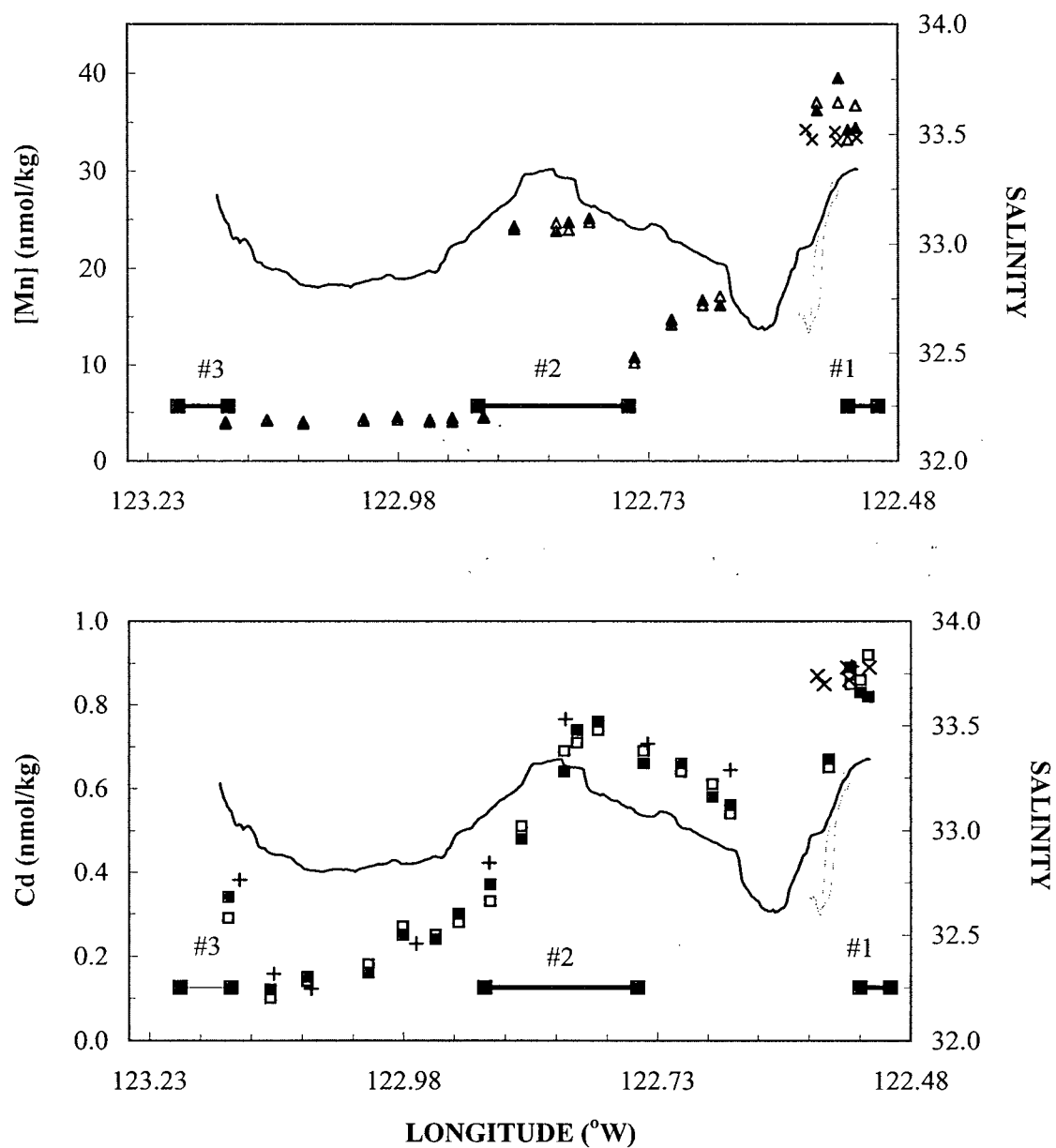


Figure 3.6.3.3

Trace metal data for WCSST 03.

(Legend: solid line = salinity; open/closed  $\blacktriangle$  = Mn replicates; open/closed  $\blacksquare$  = Cd replicates; open/closed  $\blacksquare$  = Cd replicates; + = Cd UCSC data; # = upwelling regime; X = 'dog-leg' data)

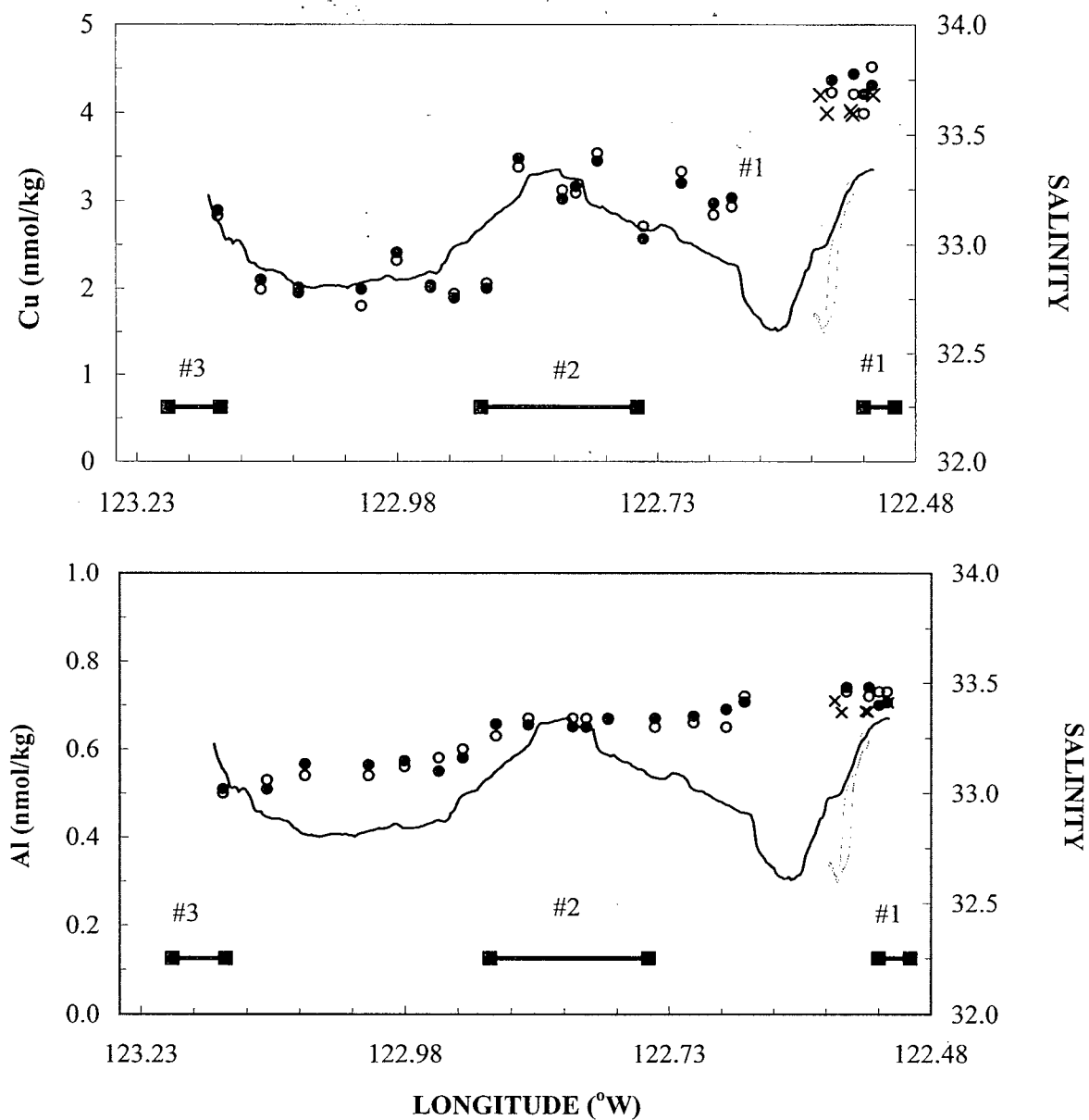


Figure 3.6.3.3

Trace metal data for WCSST 03.

(Legend: solid line=salinity; open/closed  $\bullet$  = Cu replicates; open/closed  $\blacklozenge$  =Al replicates;  
# = upwelling regime; X = 'dog-leg' data)

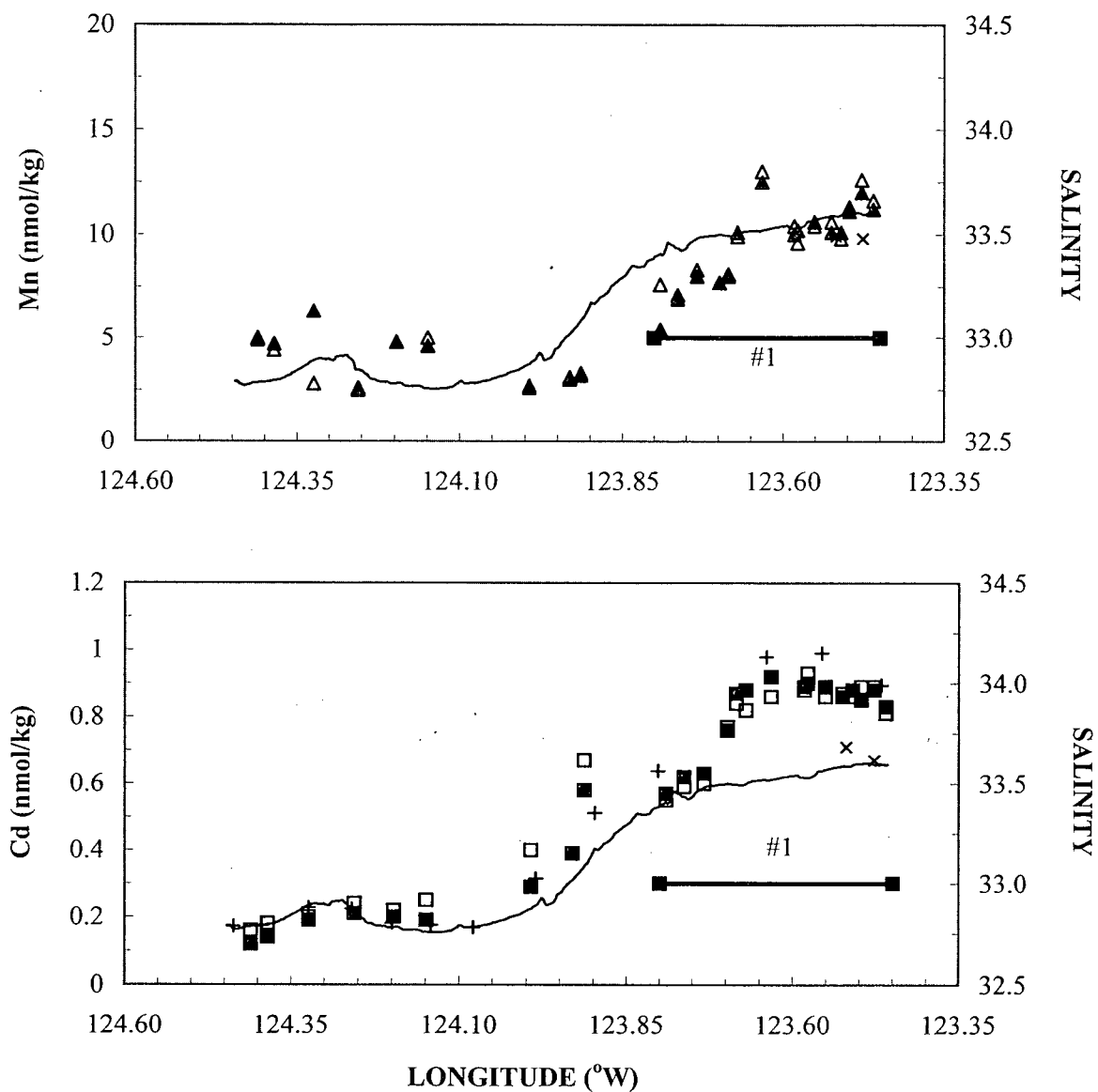


Figure 3.6.3.4

Trace metal data for WCSST 04.

(Legend: solid line = salinity; open/closed  $\blacktriangle$  = Mn replicates; open/closed  $\blacksquare$  = Cd replicates; + = Cd UCSC data; # = upwelling regime; X = dog-leg data)

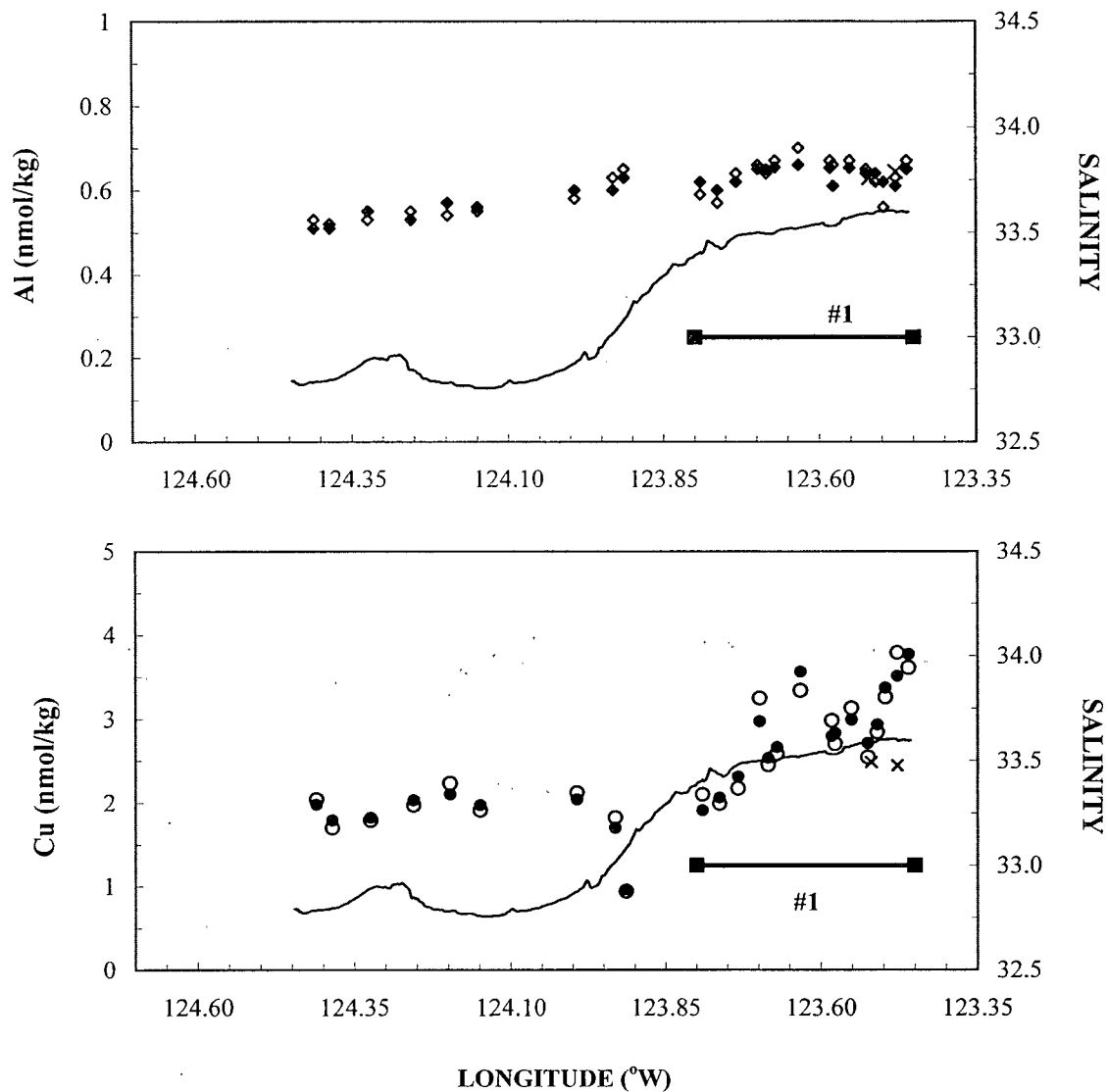


Figure 3.6.3.4

Trace metal data for WCSST 04.

(Legend: solid line = salinity; open/closed  $\diamond$  = Al replicates; open/closed  $\bullet$  = Cu replicates; # = upwelling regime; X = dog-leg data)



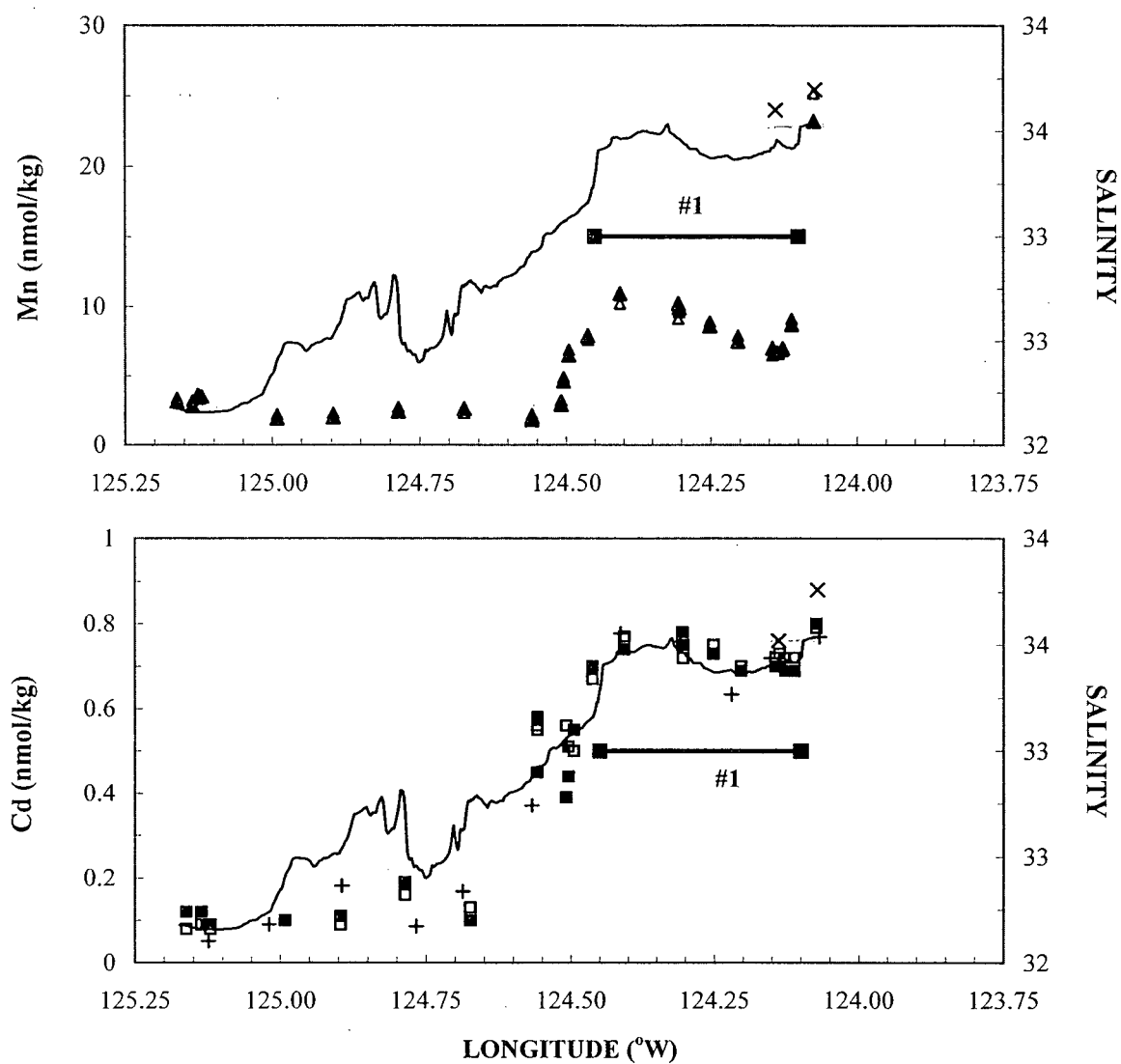


Figure 3.6.3.5

Trace metal data for WCSST 05.

(Legend: solid line = salinity; open/closed  $\blacktriangle$  = Mn replicates;  
open/closed  $\blacksquare$  = Cd replicates; + = Cd UCSC data; # = upwelling regime; X = dog-leg data)

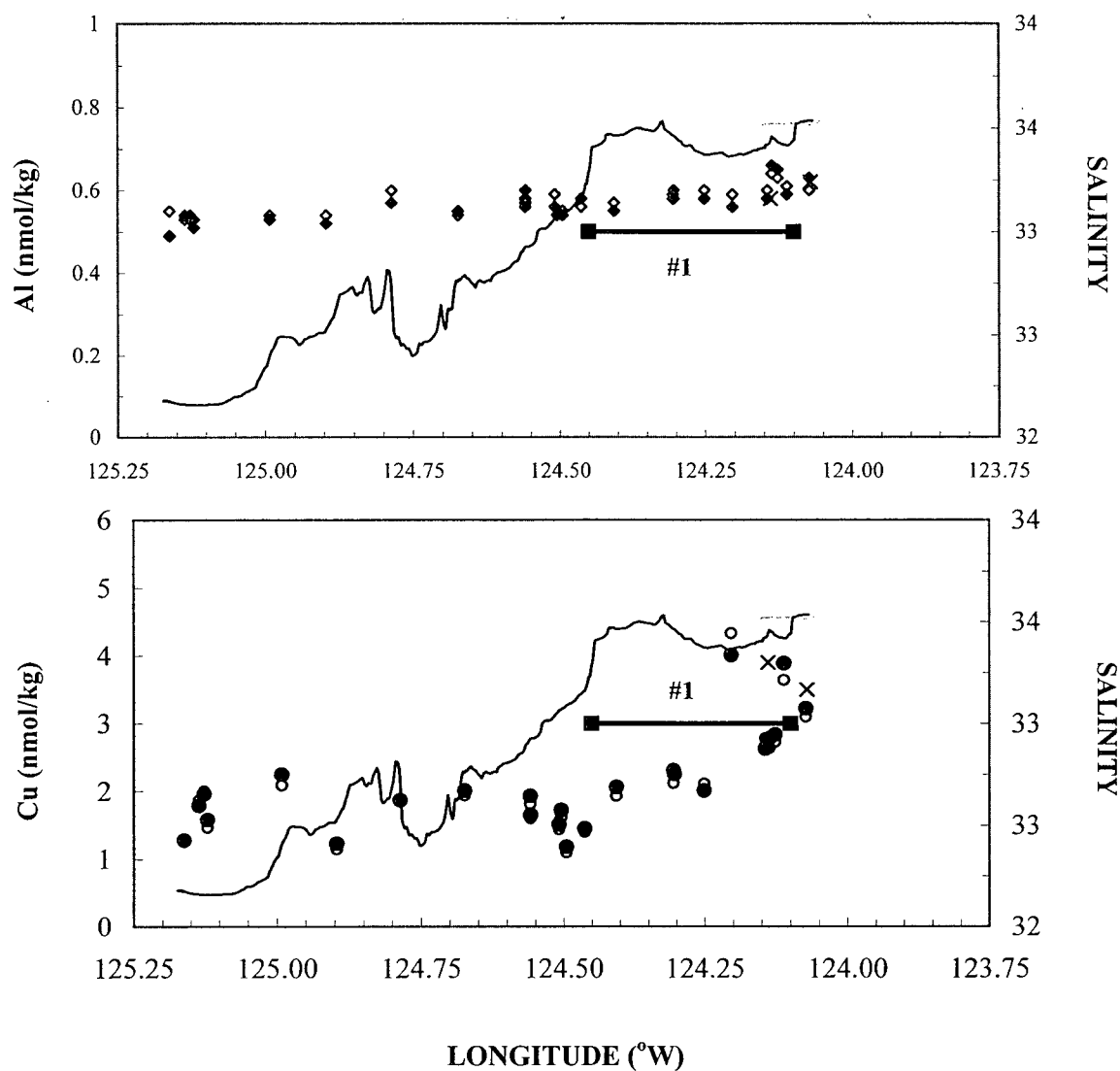


Figure 3.6.3.5

Trace metal data for WCSST 05.

(Legend: solid line = salinity; open/closed  $\diamond$  = Al replicates; open/closed  $\bullet$  = Cu replicates  
 # = upwelling regime; X=dog-leg data)

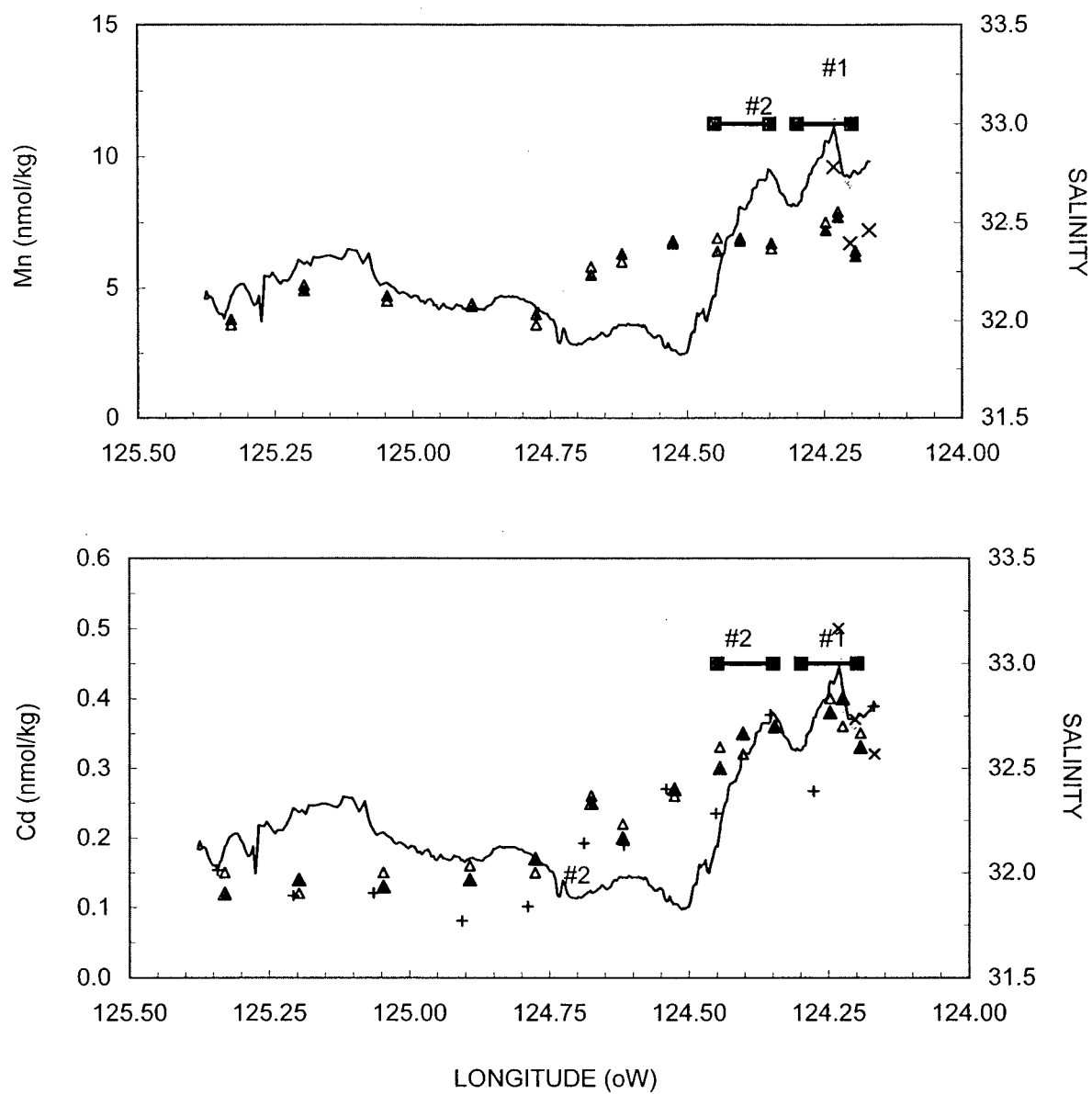


Figure 3.6.3.6

Trace metal data for WCSST 06.

(Legend: solid line = salinity; open/closed  $\blacktriangle$  = Mn replicates; open/closed  $\blacksquare$  = Cd replicates; + = Cd UCSC data; # = upwelling regime; X = "dog-leg" data)

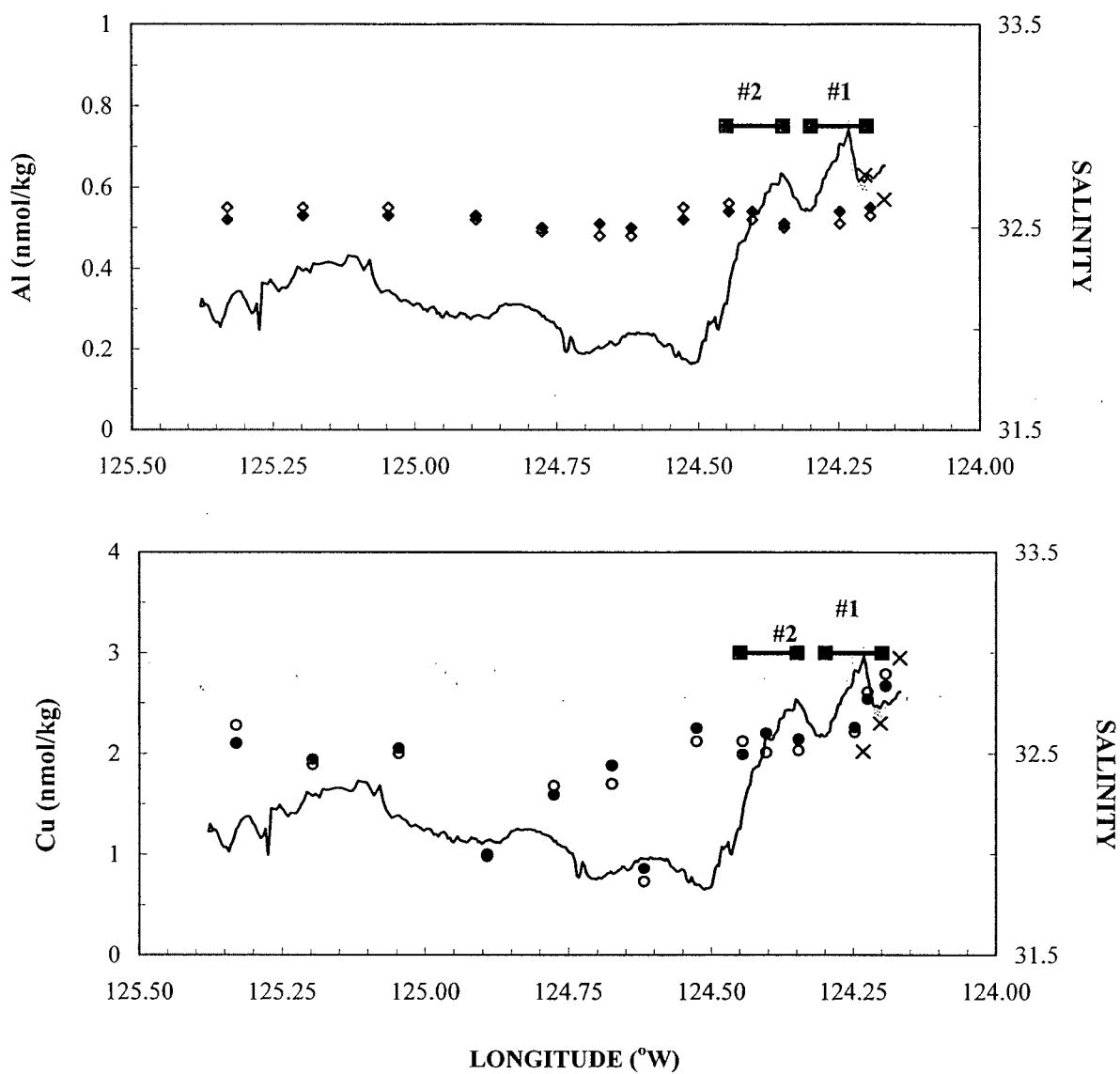


Figure 3.6.3.6

Trace metal data for WCSST 06.

(Legend: solid line = salinity; open/closed  $\diamond$  = Al replicates; open/closed  $\bullet$  = Cu repl  
 # = upelling regime; "dog-leg" data)

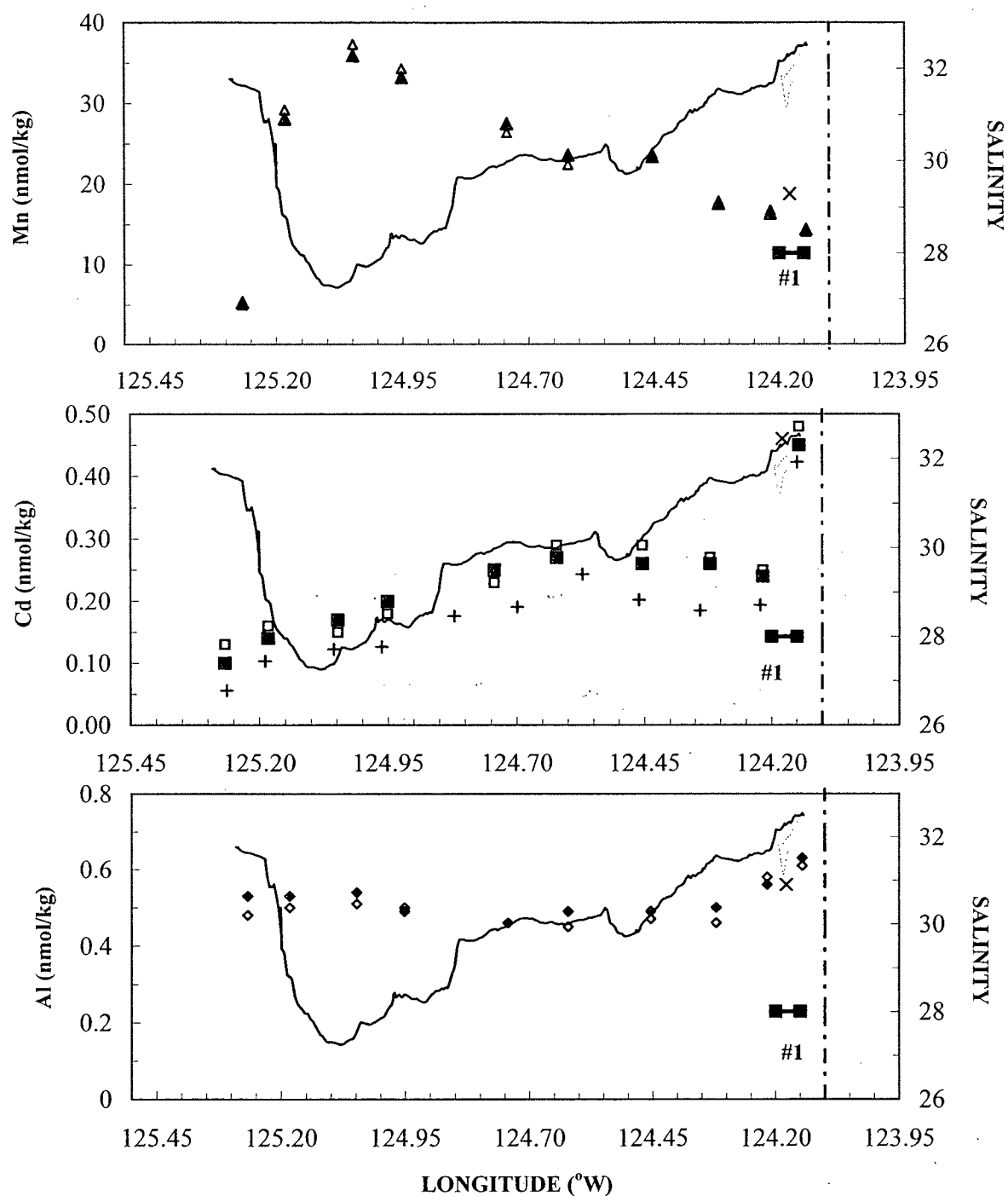
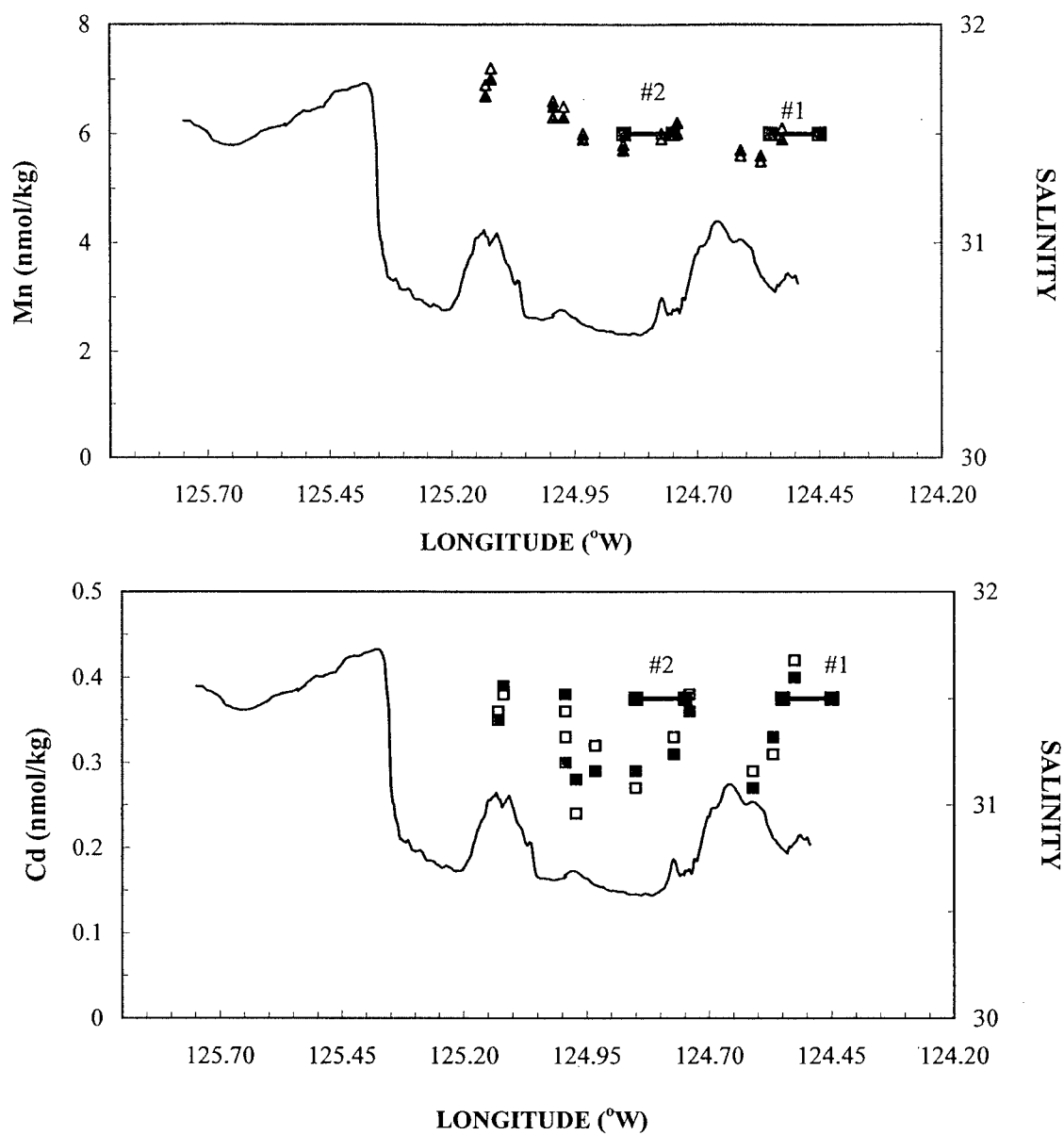


Figure 3.6.3.7

Trace metal data for WCSST 08.

Legend: solid line = salinity; ▲ = Mn replicates; ■ = Cd replicates; + = Cd (UCSC data); ◇ = Al replicates; # = upwelling regime; X = "dog-leg" data)



**Figure 3.6.3.8**

**Trace metal data for WCSST 10.**

**(Legend: solid line = salinity; open/closed ▲ = Mn replicates; open/closed ■ = Cd replicates; # = upwelling sites)**

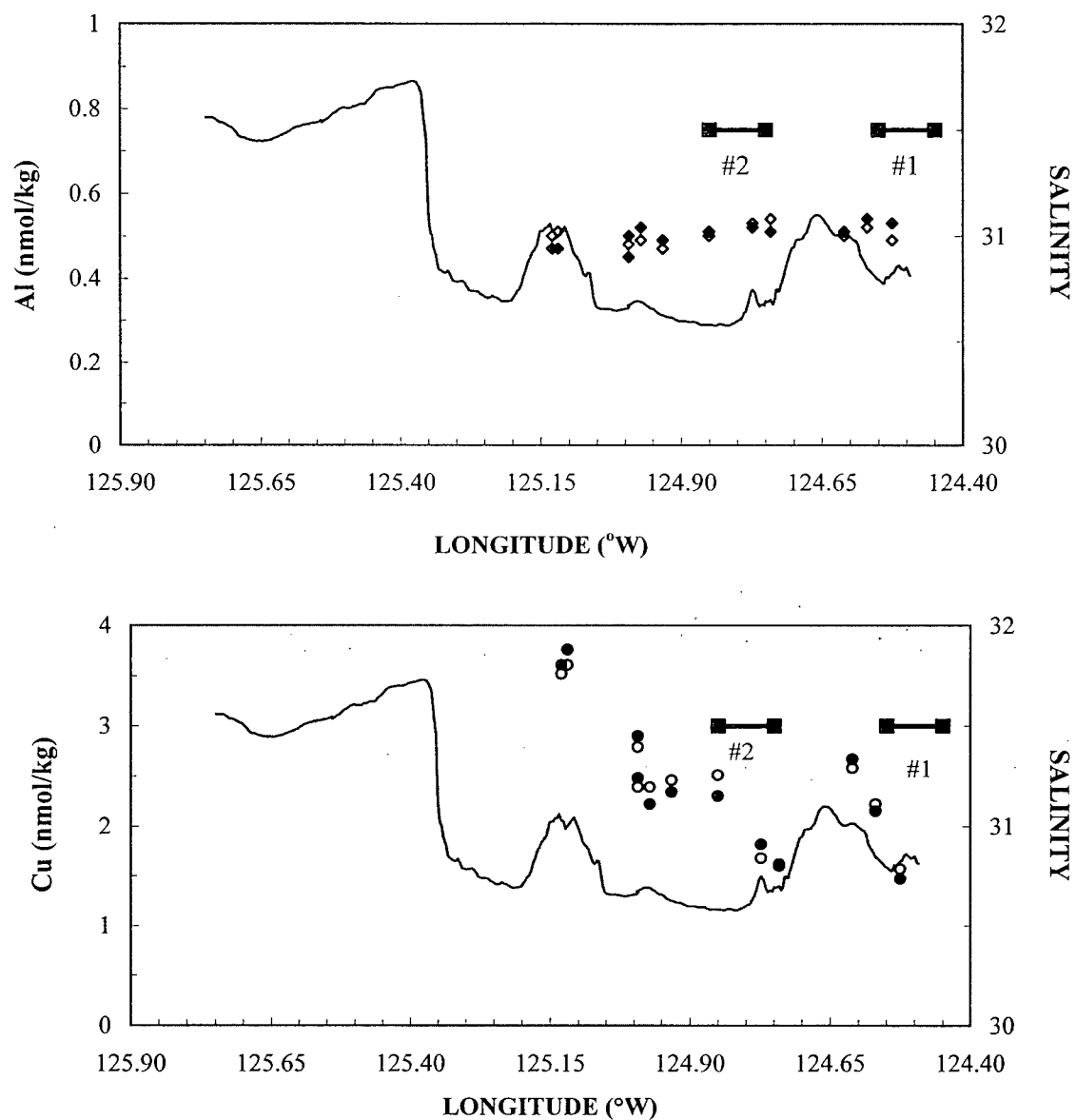


Figure 3.6.3.8

Trace metal data for WCSST 10.

(Legend: solid line = salinity; open/closed  $\diamond$  = Al replicates; open/closed  $\bullet$  = Cu replicates; # = upwelling sites)

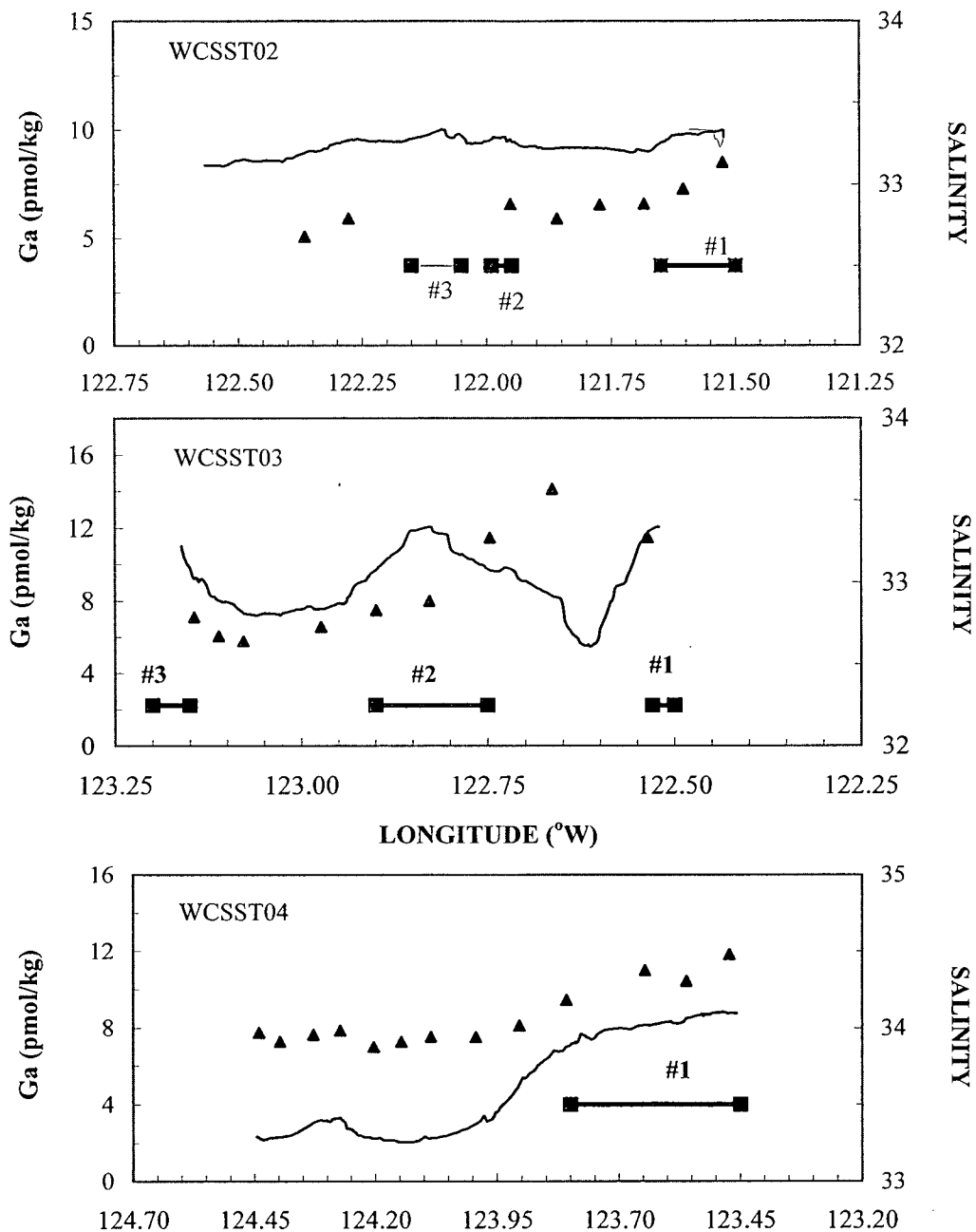
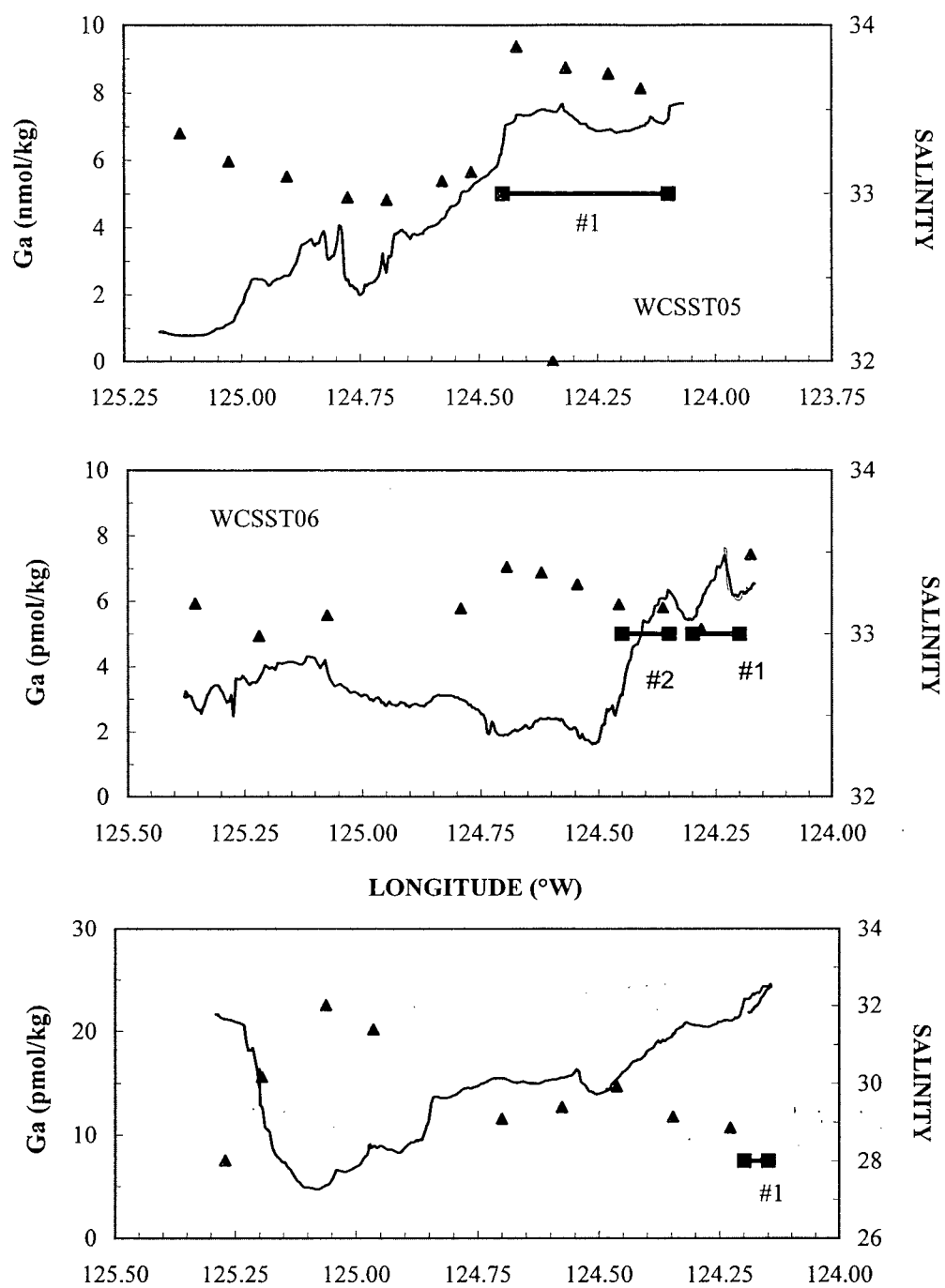


Figure 3.6.3.9

Ga data for WCSST02, WCSST03, and WCSST04

(Legend: solid line = salinity; open/closed  $\blacktriangle$  = Ga; # = upwelling regime)





**Figure 3.6.3.9**

**Ga data for WCSST05, WCSST06, and WCSST08**

**(Legend: solid line = salinity; open/closed ▲ = Ga; # = upwelling regime)**

### 3.6.5 WCSST02

Low temperature and elevated nutrient signals suggest three upwelling regions at (#1: 121.50-121.65°W; #2: 121.95-121.99°W; #3: 122.05-122.15°W). Salinity and Chl. a data sets are somewhat ambiguous however, as signals remain relatively constant across the entire transect.

Mn and Cu show a very slight elevation coincident with upwelling regime #1. Concentrations for the rest of the transect remain relatively constant and at background level. Cd shows elevation coincident with all three upwelling centers, with highest values observed at #1 and slightly lower signals at #2 and #3. Concentrations then decrease to background. "Dog-leg" signals for Mn, Cd and Cu are slightly lower than outbound leg signals observed at similar locations, suggesting more pronounced upwelling at the outbound locations. Al concentrations are constant and at background across the entire transect. Al "dog-leg" signals are very similar to outbound signals. Ga shows slight enrichment coincident with upwelling regime #1 and then remains constant at background.

### 3.6.6 WCSST03

WCSST03 shows three upwelling regions at (#1: 122.53°W; #2: 122.75-122.90°W; #3: 123.15-123.20°W). Nutrient signals are highest in upwelling regime #1; Chl. a data shows a bloom slightly further offshore. In contrast, regimes #2 and #3 both have lower nutrient signals and concurrent Chl. a blooms. Typically, there is time lag between supply of nutrients to surface water, uptake and the subsequent Chl. a bloom. Recent upwelling events are thus characterized by high nutrient signals and very little Chl. a, whereas older events exhibit lower nutrient signals and a discernible Chl. a signal. In this transect, the near shore upwelling event (#1) is probably the most recent upwelling event while older, possibly advected water from the north is responsible for the offshore signals.

Mn shows elevated concentrations at regimes #1 and #2, and a concentration minimum between the two upwelling sites. Signals at regime #3 are at background. Cd shows highest elevation at regime #1, a slightly lower elevation at regime #2 and a single

elevated signal coincident with regime #3. Cu shows significant elevation coincident with regime #1 and slightly lower elevation at regime #2 and #3. Al shows a slight elevation at regime #1; concentrations then decrease very gradually in the offshore direction to background. "Dog-leg" data for Mn, Cd, Cu and Al are comparable with outbound data for similar locations. Ga data show highest elevation at regime #1, lower concentrations at regime #2 and signals at background level for regime #3.

#### 3.6.7 WCSST04

WCSST04 indicates one nearshore upwelling regime (#1: 123.45-123.80°W). Temperature is low, salinity and nutrient signals are high. Chl. a shows two blooms located further offshore than the upwelling regime.

Mn, Cd, and Cu are all enriched in the upwelling region; concentrations then decrease slowly offshore to background. "Dog-leg" signals for Mn, Cd and Cu are slightly lower than corresponding outbound signals, suggesting that the upwelling event was more pronounced during the outbound leg of the transect. Ga shows elevation in the upwelling center and the same slow decrease to background values offshore. Al shows a gradual decline in concentration in the offshore direction; however it is difficult to justify stating that this decline suggests significant elevation close to shore in a manner akin to the other metals, as signals in the eastern sector are only very slightly elevated above background.

#### 3.6.8 WCSST05

Low temperature and elevated salinity and nutrient signals suggest a single upwelling regime close to the shore (#1: 124.1-124.45°W) for WCSST05.

The Mn distribution shows some complexity within the upwelling region with signals initially high, then showing a decrease but still remaining above background before increasing slightly. Outside the upwelling zone concentrations are fairly uniform and at background. Cd shows elevation coincident with upwelling and then a decrease to background. Cu shows elevation in the upwelling regime followed by a decline to background. Cu signals are somewhat variable within the upwelling regime. Al signals are at background across the transect though there does appear to be a general trend of

higher values in the eastern sector followed by a very gradual decline toward the west. "Dog-leg" signals are comparable for all metals with corresponding outbound signals. Ga shows elevation coincident with the upwelling regime, a slow decrease to background in the offshore direction and a slight increase at the far western end of the transect.

### 3.6.9 WCSST06

WCSST06 is somewhat of an anomalous transect. Low temperature and elevated salinity signals suggest the presence of two upwelling regimes (#1: 124.2-124.30° W; #2: 124.35-124.45° W). Nutrients, however, show no response. Enhanced Chl. a. signals suggest that a localized bloom is underway at regime #1. It would appear that the upwelling event at regime #1 is old and that nutrients had been stripped out of the water by the time we sampled. Salinity offshore is slightly lower than values observed for transects south of WCSST06. This could be explained by dilution from advected plumes of Rogue River water. However, Huyer (1983) and streamflow data from the United States Geological Survey (Rogue River discharge for June 1997: 4000 ft<sup>3</sup>/s; July 1997: 2880 ft<sup>3</sup>/s) suggest that there is virtually negligible discharge from the Rogue River for the time period of this study.

Mn, Cd and Cu show slight elevation in regimes #1 and #2; and concentrations for all gradually decrease offshore to background. Al again shows no elevation above background across the entire transect. Again, "dog-leg" signals are comparable with those observed on the outbound leg of the transect. Ga shows slight elevation close to shore (regime #1) and a decrease in the offshore direction.

### 3.6.10 WCSST08

WCSST08 shows one upwelling event close to the shore (#1: 124.15-124.20). Salinity and nutrients are elevated; and Chl. a shows a bloom concurrent with the upwelling region indicating that the event was not recent.

Mn and Cd show elevation coincident with the upwelling regime. Al shows no elevation coincident with the upwelling regime. No Ga or Cu data are available for this transect. Note that the elevation towards the western sector of the transect will be discussed in the next chapter.

### 3.6.11 WCSST10

Temperature, salinity and nutrient data suggest the presence of two upwelling regions (#1: 124.75-124.85°W; #2: 125.20-125.35°W). However, the magnitude of nutrient elevation is significantly less, and the temperature signal higher, than that seen for other transect upwelling sites.

Mn, Cd and Cu show elevation coincident with all upwelling sites. Al signals are at background across the entire transect. No Ga data are available for this transect.

## 3.7 Discussion

### 3.7.1 Introduction

The purpose of this work was to assess the impact of oceanic (upwelling) and benthic sources on trace metal concentrations. Upwelling regimes were identified through the use of salinity, temperature and nutrient data, where low temperature, elevated salinity and nutrient signals clearly indicate upwelling sites. In addition, Chl.a data in conjunction with nutrient data, give an indication of the age of the upwelled water, with recent upwelling events typically characterized by high nutrient signals and very low Chl. a signals, and older events exhibiting lower nutrient signals and a discernible Chl. a signal. In these upwelling regimes, metals with benthic/bottom water sources are expected to show surface water elevation as metal-rich bottom waters are transported to the surface by the upwelling. As Mn, Cu, Cd and Al (potentially) have bottom water sources, these metals were expected to show elevation above background California Current surface water values coincident with upwelling regimes. In addition, a strong correlation between shelf width and signal magnitude for those metals whose distributions are impacted by sediment sources (Mn, Cu and Al) and a correlation between the strength of the upwelling and signal magnitude were expected.

With the exception of Al, all metals are enriched in upwelled waters (Mn: 4.6-39.5nmol/kg; Cd: 0.32-0.92nmol/kg; Cu: 1.66-4.52nmol/kg) compared with California Current surface waters (Mn: 3-5nmol/kg; Cd: 0.08-0.30nmol/kg; Cu: 0.79-1.62nmol/kg). Both Mn and Cd show very clearly defined elevation coincident with the upwelling regimes; for those transects with only one upwelling region, they show a very distinct

decline to background values with increasing distance from the upwelling region, and for those transects with more than one upwelling regime these metals typically show concentration minima between upwelling sites. While Cu also shows elevation coincident with upwelling sites, its signals are more variable and the transition between upwelling sites is less distinct than that shown by either Mn or Cd. Al showed signs of slight elevation at only two transects (WCSST03 and WCSST04), however the difference in signal magnitude between upwelled waters and California Current offshore waters is small compared to that shown by the other metals. For all other transects, Al is at background.

### **3.7.2 Trace Metal distributions**

#### **3.7.2.1 Manganese**

The behavior of Mn conforms to expectation. It is well known that Mn has a sediment source and the enhanced Mn signals observed in this study coincident with upwelled waters are thus attributable to the transport of Mn-enriched bottom waters to California Current surface waters.

The mechanism of supply of Mn from sediments is well known (see for example Thamdrup *et al*, 1994). Mn (and Fe) oxides and hydroxides deposited in sediments are reduced upon burial below the oxic boundary and  $Mn^{2+}$  (and  $Fe^{2+}$ ) subsequently diffuses upwards toward the sediment-water interface. The redox state of the sediment will play a crucial role in determining the extent of the  $Mn^{2+}$  flux to pore waters. For significant release of  $Mn^{2+}$  to the water column to occur from coastal sediments, the rate of Mn oxidation in the sediment must be exceeded by the rate of Mn reduction that supplies  $Mn^{2+}$  from below. If this is not the case, then most of the upwardly diffusing  $Mn^{2+}$  will be oxidized back to the solid state upon contact with  $O_2$  and  $MnO_2$  will be trapped at the redox boundary producing a total Mn maximum. Reaction with carbonate ( $CO_3^{2-}$ ) will also precipitate Mn out of solution, again producing a total Mn maximum.

Mn may also be produced through degradation of particulate organic carbon (C) and calcium carbonate ( $CaCO_3$ ). For example, Johnson *et al* (1992) examined the flux of Mn from continental sediments across the shelf and slope of the California margin during June 1991, when the area was subject to significant upwelling. These authors reported

substantial benthic Mn fluxes and attributed them, in part, to the remineralization of Mn associated with particulate C and  $\text{CaCO}_3$ . Johnson *et al* (1992) then went on to examine the role played by manganese oxide reduction in generating this flux. They reported an  $\text{O}_2$  penetration depth in the sediments of 25mm at 100m. It appears that while the sediments receive significant C input, they are overlain by high  $\text{O}_2$  concentrations ( $>10\mu\text{M}$ ). As dissolved Mn(II) produced in the  $\text{O}_2$  deficient region below the sediment-water interface will re-oxidize when bottom water  $\text{O}_2$  exceeds  $10\mu\text{M}$  (Shaw *et al*, 1990), only Mn released at the sediment water interface can escape the sediments. As my study was also conducted during June (and July) and was coincident with significant upwelling, it is plausible that sediments at this time had a comparable  $\text{O}_2$  penetration depth.

The elevation of Mn observed coincident with upwelled waters in this study can thus be attributed to a combination of degradation of particulate C and  $\text{CaCO}_3$ , and reduction of manganese oxides in the mildly reducing shelf sediments. Both pathways are very plausible; in coastal environments such as the Pacific Northwest coastline, a high organic matter deposition rate is to be expected and will typically cause both reducing conditions and the redox boundary to lie within a few millimeters to a few centimeters of the sediment water interface (see for example Thramdrup *et al*, 1994; Johnson *et al*, 1995; Heggie *et al*, 1987; Hedges *et al*, 1999). While I did not obtain  $\text{O}_2$  penetration depth data for this cruise, Johnson *et al*'s work suggest that a depth of about 25mm would be a reasonable estimate. In addition, several other authors have reported reducing shelf conditions for this region (see for example Hedges *et al*, 1999; Sanudo-Wilhelmy and Flegal, 1996; van Geen and Luoma, 1993), and attributed elevated metal concentrations to fluxes from these sediments. This again supports the idea that the shelf was in a reduced state during the cruise, with the redox boundary lying within a few centimeters of the sediment-water interface.

#### 3.7.2.2 Cadmium and Copper

On examining typical vertical profiles of Cd and Cu (see for example Chapter 1, sections 1.2.3, 1.2.4), it becomes clear that these elements participate in a biogeochemical cycle of removal by phytoplankton from surface and near-surface waters, and subsequent regeneration from falling biological debris into solution with depth. The regeneration

depth varies for each metal, with Cd being regenerated at shallow depths and Cu at or near the bottom. As both metals show this increase in concentration with depth, it is plausible that the elevation of Cd and Cu observed in upwelled waters, is attributable, at least in part, to the transport of this enriched deeper water to the surface by upwelling. However, while several authors have attributed elevated Cd signals to the upwelling of this deeper water source (see for example Bruland 1980; Boyle *et al*, 1981), there remains a question as to whether Cu will indeed show significant elevation by this mechanism in coastal waters. For example Boyle *et al* (1977, 1981), Bruland and Franks (1983) and Rutgers *et al* (1997) all suggested that because the concentration gradient of Cu in the upper ocean is so small in comparison to other trace metals, coastal upwelling, which draws its water from depths just below the thermocline, will not have a significant impact on coastal surface water signals.

Cu may also have a benthic source; several authors (see for example Saager *et al*, 1997; Sanudo-Wilhelmy and Flegal, 1996; van Geen and Luoma, 1993; Westerlund *et al*, 1991) have suggested that continental shelves may act as a source of dissolved Cu to overlying waters through diagenic remobilization from mildly reducing terrigenous sediments (even though Cu itself, unlike Mn or Fe for example, is not mobilized by reduction). Gibbs (1977) reported that terrigenous sediments, subject to oxic conditions, typically contain significant quantities of Cu strongly bound by iron and manganese oxides. Once  $O_2$  is depleted, alternate oxidation pathways, involving Mn and Fe oxyhydroxides and oxides, dominate.  $Fe^{2+}$  and  $Mn^{2+}$  are released into sediment pore waters and any trace metal bound up in the oxides is presumably also released into solution and is thus able to migrate upwards by diffusion. The redox state of the sediment now becomes crucial in determining the extent of dissolved Cu flux to overlying waters. If the sediment is only mildly reducing, a significant amount of dissolved Cu can still be trapped when  $Mn^{2+}$  diffusing upwards interacts with  $O_2$  and gets reduced back to Mn oxides and oxyhydroxides which can then re-trap dissolved  $Cu^{2+}$ . Significant amounts of dissolved Cu may also be released through the degradation of organic matter or from particulate calcium carbonate (see for example Johnson *et al*, 1992; Martin and Knauer, 1983). Work by Sanudo-Wilhelmy and Flegal (1996) off Baja California and van Geen and Luoma (1993) off San Francisco Bay attribute elevated Cu



concentrations to fluxes from reducing shelf sediments agreeing well with my data. The elevation of Cu coincident with upwelled waters observed in this study is thus governed by similar conditions to that required by Mn; reducing shelf sediments that cause the release of Cu bound up in Fe and Mn oxyhydroxides, and the degradation of particulate carbon and calcium carbonate.

In light of the behavior described above, the observed response of Cd and Cu to upwelling regimes makes sense. Both metals show significant elevation in upwelling waters and a decline to background with increasing distance from the upwelling. As Cd is not known to have a benthic source, its response is expected to be less effected than that of Cu by the changing continental shelf width. This appears to be the case, with both metals showing a correlation between shelf width and signal magnitude, and Cd showing less response to the changing shelf width than Cu (see table 3.6.3.1). For example, at WCSST02 (where the continental shelf is very narrow), it is interesting to note that while the signal magnitude for Cd in upwelled waters at this transect was significantly lower than was seen at other locations, it was still elevated well above background; in addition elevation was observed at all three upwelling regimes. This is in contrast to Cu (also Mn and Ga) where the elevation was barely above background and was only observed for the upwelling regime closest to shore. The other significant difference between the behavior of Cd and Cu is the occasional variability in the Cu data. A similar degree of variability has been reported by several authors including Rutgers van der Loeff (1997) who observed elevated but highly variable values of Cu in upwelled waters off Namibia.

Several authors have reported Cd data from locations close to some of the stations sampled in this work; in addition Bruland (personal communication) provided Cd data obtained by his laboratory at the University of California at Santa Cruz during this cruise (Bruland's samples are taken from similar locations to mine but are fewer in number). My Cd data show excellent agreement with this work. For example, van Geen and Husby (1996) reported Cd surface water values from June 1991-1993 up to about 0.6nmol/kg at locations very close to WCSST04, up to about 0.53nmol/kg at locations close to WCSST03, and about 0.25nmol/kg at locations close to WCSST02. Although my values are higher than van Geen's, it is likely that upwelling was more intense (due extremely windy conditions) in June/July 1997 compared with June 1991-1993. My data

also agree very well with Bruland's data both in terms of relative and absolute values, and the two data sets together provide a detailed map of dissolved Cd off the NE Pacific coast. Bruland's data also show elevation coincident with upwelling centers, with highest values observed at WCSST03 and 04, intermediate at WCSST05 and lowest at WCSST02.

### 3.7.2.3 Aluminium

Al shows signs of very slight enrichment in upwelled waters at transects WCSST03 and WCSST04 only, with a very small difference in signal magnitude between upwelled waters and California Current offshore waters compared to that shown by the other metals. For all other transects, Al typically exhibits higher signals nearshore followed by a very gradual decline in the offshore direction, with all signals in the background range.

The results were somewhat unexpected; while Al does not undergo diagenesis, several authors have proposed sediments as a potential source of Al to overlying waters and on this basis I had anticipated that the metal would show a more marked response to upwelling than was observed.

If sediments do indeed act as a source of Al to overlying waters, then even given the shorter surface water resident time of Al versus Mn, Cu and Ga, I expected to observe some sign of elevation coincident with upwelling regimes in a manner akin to that seen for the other metals. The fact that Al was, for the most part, at background, suggests either that sediments in this region do not act as a significant source of Al or that Al is supplied by the sediments but is then stripped out of the water at a dramatic rate. With regard to the latter explanation, it is interesting to compare these data with Fe data supplied by Bruland (personal communication), and here, again the results were surprising. In contrast to Al, Fe does show elevation above background coincident with upwelling regimes at WCSST03, 04 and 05 and to a lesser extent at WCSST02, followed by a decline to background in the offshore direction. If Al is being supplied by sediments then it must be subject to removal from California Current waters at a faster rate than not just Mn, Cu and Ga but also Fe; and this certainly agrees with the results obtained for waters impacted by the Columbia River, where again Al is removed significantly faster than other metals (see chapter 4).

### 3.7.3 Impact of Shelf Width

Mn, Cu, and to a lesser extent Cd and Al, show a strong correlation between signal magnitude and location (see table 3.6.3.1). Mn shows highest values coincident with upwelled waters at WCSST03, intermediate values at WCSST04, WCSST01 and WCCST08 and lowest values coincident with upwelling at WCSST02, WCSST06 and WCSST10. WCSST05 is somewhat ambiguous; within the upwelling regime close to shore I recorded two very high signals followed by signals that were elevated above background but considerably lower. Cu showed greatest elevation coincident with upwelling regimes in WCSST03 and WCSST05, intermediate values at WCSST04 and WCSST10, and lowest values at WCSST01, WCSST02 and WCSST06. Cd data showed highest values coincident with upwelled waters at WCSST01, WCSST03, WCSST05 and WCSST08 and intermediate values at WCSST02, WCSST04, WCSST06 and WCSST10. Al signals were highest coincident with WCSST03 and WCSST04 (indeed these were the only transects where Al showed elevation above background).

A similar correlation between signal magnitude and location was observed by Hutchins and Bruland (1998) and Bruland (personal communication) for Fe and by Lanthier (1998) for Ga. Data obtained during the 1997 West Coast cruise by Hutchins and Bruland (1998) and Bruland (personal communication) focusing on Fe (which is subject to both post depositional remobilization and resuspension in an analogous manner to Mn) reported the Pacific northwest continental shelf as an important source of Fe to surface waters. The highest Fe signals were observed coincident with upwelled waters at WCSST03 and WCSST04, the lowest at WCSST02 and intermediate at WCSST01 and WCSST05. Interestingly, for the upwelling regime at WCSST05, Fe also exhibits significantly higher (three times higher) signals close to the shore than those near to the upwelling/California Current water front. Ga, while not involved in redox cycling, is known to exhibit deep water regeneration similar to sediment resuspension or diagenesis. Data supplied by Lanthier (1998) show Ga concentrations elevated in upwelling regimes with highest concentrations observed at WCSST03, WCSST04 and WCSST05, and the lowest at WCSST02 and WCSST06.

These findings indicate that Mn, Cu, Fe and Ga levels are correlated with shelf

width, with levels in the Big Sur area (WCSST02), where the shelf is extremely narrow, approaching those found in background California Current waters. North of Monterey Bay where the shelf widens, signals for all four metals increase significantly with the greatest increase typically observed at WCSST03 and WCSST04 where the shelf is widest. WCSST05 is difficult to constrain for Mn, Cu and Ga due to the complexity of the signal within the upwelling zone; all metals show high signals (comparable to those seen at WCSST03 and WCSST04) close to the coast followed by a decrease to intermediate concentrations toward the upwelling/California Current boundary; this possibly reflects an initial upwelling of shelf waters followed by upwelling of waters no longer in contact with the shelf. Interestingly, Fe also exhibits significantly higher (three times higher) signals close to the shore at this transect than those near to the upwelling/California Current water front.

The results strongly support the contention that resuspension or diffusion from shelf dissolved Mn, Cu (and Ga and Fe) to overlying waters. However, it is important to realize that concluding directly from these data alone, that shelf width is the controlling factor on metal signal magnitude, is somewhat simplistic. Upwelling intensity and the age of upwelled waters may also exert a control on signal magnitude. It is interesting to note that while the signal magnitude for Cd does vary to an extent with location, the variation is less than that seen for other metals. This is particularly noticeable at WCSST02 where the shelf is very narrow. Here, Mn, Cu, Al, Ga and Fe all exhibit signals that are at background or barely above background. While Cd does exhibit a lower elevation at this transect compared to WCSST03 or WCSST04 where the shelf is significantly wider, the elevation seen for Cd at WCSST02 is still comparatively higher than that seen for the other metals. This makes sense in terms of the behavior of Cd; Cd does not have a benthic source, instead the observed elevation in upwelled waters is attributed to transport of enriched deeper water to the surface by upwelling. Thus, one would not expect elevation of Cd to be as strongly dependent on shelf width as Mn or Cu, both of which have a strong shelf source.

#### 3.7.4 Intensity of Upwelling and Age of Upwelled Waters

Several of the transects contain upwelling regimes that differ in intensity and/or age, and I anticipated seeing a response to these differing regimes by the trace metals. For example, at WCSST01 there are two upwelling regimes, one close to the shore (#1) and the other further offshore (#2). It is likely that the near-shore event is derived from older, advected upwelled water from Ano Nuevo just to the north of Monterey Bay which has been depleted of its nutrients and warmed. Interestingly, Mn, Cd and Cu all show significantly higher signals coincident with the newer regime (#2) compared with those recorded for the older regime (#1). Presumably these older waters have been stripped of their trace metals and nutrients over time. At WCSST03, it is interesting to compare regimes #1 and #2. The nutrient signals for regime #1 are higher than those seen at regime #2. This probably reflects either stronger upwelling at regime #1 relative to that at regime #2 or that regime #2 is an older event than regime #1; trace metal data appear to fit either scenario well with Mn, Cd, and Cu showing significantly higher elevation at regime #1 compared with regime #2. At WCSST06, low temperature and elevated salinity signals suggest the presence of two upwelling regimes. However, nutrients show no response, and the trace metals show only very slight elevation above background – indeed their signals are comparable in magnitude to those recorded at WCSST02. Chl.a data show a response coincident with the regimes #1 and #2. It is therefore likely that if upwelling occurred at this location, it must have taken place prior to the time at which we sampled. Thus, by the time we reached the site, nutrients and trace metals had been partially stripped out of the water resulting in the observed Chl.a bloom. For WCSST08 and WCSST10, temperature and salinity data suggest the presence of upwelling, however in both cases nutrient signals - though higher than those at WCSST06 - are significantly lower than those at WCSST01-05 suggesting intermediate strength upwelling. Again, trace metal data are consistent with this idea, with signals intermediate in magnitude.

### 3.8 Summary

Upwelling events occurring off the coasts of California, Washington and Oregon during June/July 1997 were clearly identified by characteristic low temperature, high salinity and high nutrient signals.

Upwelled waters contained elevated levels of Mn, Cd and Cu (Mn: 4.6-39.5nmol/kg; Cd: 0.32-0.92nmol/kg; Cu: 1.66-4.52nmol/kg) compared with California Current surface waters (Mn: 3-5nmol/kg; Cd: 0.08-0.30nmol/kg; Cu: 0.79-1.62nmol/kg). Al showed very slight elevation coincident with WCSST03 and 04 only (0.63-0.74nmol/kg); all other transects were at background (0.38-0.65nmol/kg). Both background and upwelling data agrees well with previous work by other authors.

The data make it abundantly clear that diagenic remobilization and sediment resuspension coupled with upwelling provide an important source of Mn and Cu (and Ga) to surface coastal waters of the California Current. Cd probably does not have a benthic source; however vertical profiles of Cd typically show an increase in concentration with depth, thus the elevation of Cd observed in this study coincident with upwelled waters is most likely attributable to the transport of this enriched deeper water to the surface by upwelling. The Al results were somewhat unexpected in that they did not show the anticipated upwelling signature observed for the other metals. This suggests either that sediments in this region do not act as a significant source of Al or that the Al supplied by the sediments is stripped out of the water at a dramatic rate – faster than that seen for Mn, Cd, Cu, Ga or Fe.

Mn, Cu (Cd and Al to a lesser extent) showed a very tight correlation with shelf width with highest signals observed where the shelf was widest (WCSST03-05) and lowest where the shelf was narrow (WCSST02). This agrees well with Fe and Ga data supplied by Bruland & Hutchins and by Lanthier, respectively, which also suggests a correlation between shelf width and signal magnitude. It is interesting to note that the Cd signal magnitude was not as dependent on shelf width; presumably this reflects the fact that Cd elevation is attributable primarily to upwelling of Cd-enriched bottom water and is not dependant on benthic sources.

For those transects that contained upwelling events that varied in age or intensity; trace metal and nutrient signals typically showed great elevation coincident with newer

and/or more intense upwelling events. As nutrients are drawn down, and Chl. a is produced, trace metals are removed from the waters through a combination of active uptake and/or passive adsorption.

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## Chapter 4: The Columbia River as a Source of Mn, Al and Cd to the California Current System

### 4.1 Introduction

#### 4.1.1 Riverine and Estuarine Dynamics

Rivers are a major source of trace metals to the oceans (Sholkovitz, 1976, 1978). The contribution from this source is often significantly altered in estuarine and continental shelf environments. It is here that physical, chemical and biological processes combine to substantially modify the riverine flux of dissolved material to the ocean (Taylor *et al.*, 1990; Shiller and Boyle, 1991, 1987; Shiller, 1988). A clear understanding of the geochemical dynamics of estuaries is therefore an essential step to determining metal mass balances for the coastal region in particular and for the oceans in general. Many trace metals are significantly impacted by estuarine processes. For some (e.g. Na, Ca, K), the estuary is a simple chemically conservative mixing zone between the river and the ocean. For others, the estuary may act as either a source or sink, supplying or removing via biological and chemical means varying fractions of the metal (Shiller and Boyle, 1991, 1987; Shiller, 1988).

In river water, metals may be present in the dissolved state as ionic, hydrated inorganic forms or organically associated forms; and in the particulate state as organically bound, lattice bound or co-precipitated forms. As river water mixes with saline sea water shifts in pH, increases in specific ions such as  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ , and an increase in overall ionic strength from 0 to 0.7 alter the dissolved speciation of metals and the adsorption behavior of riverine particles (Martin and Whitfield, 1983). Metals may undergo a variety of reactions such as flocculation, sedimentation, co-precipitation in association with humic acids, clay minerals or Fe and Mn oxyhydroxides, and biological interaction which result in their removal to sediments (Sholkovitz, 1976, 1978). Metals that are initially removed to the particulate phase and then to the sediments may subsequently be recycled, transported and deposited to the outer estuary or to the continental shelf. Thus, estuarine sediments act as both a removal path for river borne trace metals as well as a potential source path of trace metals to the overlying water.

## 4.2 Rivers as a source of dissolved Mn, Al and Cd

### 4.2.1 Manganese

Freshwater runoff is an important source of Mn to the ocean (see for example Klinkhammer *et al*, 1997; Ponter *et al*, 1992; Cossa *et al*, 1990; Jones and Murray, 1985; Landing and Bruland, 1980). Average dissolved Mn river water concentrations of 130nmol/kg-150nmol/kg have been suggested by Martin and Whitfield (1983). Sholkovitz (1976, 1978) suggests that 25-45% of dissolved Mn may be removed during estuarine mixing and subsequently converted to a reactive particulate form. Much of this reactive Mn fraction will thus be available to return solution and this dissolution will be especially pronounced in anoxic estuarine and coastal sediments.

Several authors have investigated the impact of riverine input on levels of Mn in marine environments. Yang and Sanudo-Wilhelmy (1998) investigated Mn distributions in the Hudson River estuary. Mn concentrations (ranging from 0.033-1.46 $\mu$ M) were strongly dependent on season and discharge. Highest concentrations were detected under low freshwater discharge, implying that limited hydraulic flushing allows the build up of Mn in the water column. These authors suggested dissolved Mn estuarine budgets to be maintained through a combination of riverine input and benthic sources. Ouddane *et al* (1997) reported dissolved Mn in the Seine River estuary to be strongly influenced by increases in salinity with maximum concentration (150-170nM) coincident with low salinity waters ( $s=5-10$ ). Similar behaviour was observed by Muller *et al* (1994) in the Clyde Estuary, Scotland. Minakawa *et al* (1998) suggested input from the Yukon River was an important source of Mn to the Bering Sea. While a large quantity of particulate Mn is thought to be supplied by various Alaskan rivers (Milliman and Meade, 1990), these are assumed to be deposited rapidly in the shelf region. Jickells *et al* (1988) suggested elevated coastal dissolved Mn concentrations (approx. 3.5nmol/kg) in the Sargasso Sea reflected enhanced inputs from fluvial (and/or atmospheric) sources. Significant input to estuarine surface waters of dissolved and particulate Mn has also been reported for the Mississippi River and the Scheldt River, Netherlands, respectively (Taylor *et al*, 1990; Zwolsman and van Eck, 1999).

A somewhat limited amount of research has been undertaken on Mn distributions in the Columbia River. Klinkhammer *et al* (1997) investigated Mn distributions in the Columbia River estuary and plume during May 1994 and 1995. Surface waters in the

Columbia Estuary exhibited dissolved Mn signals as high as 98-100nM; this elevation was attributed to packets of water advected from peripheral bays adjoining the estuary just west of this section. Water in these bays has a short residence time (on the order of days) before it is flushed into the main channel and is characterized by the reduction of Mn-oxides in tidal mudflats. Elevated Mn signals were also observed toward the seaward edge of the Columbia River plume (around 40nM). This elevation was coincident with high turbidity and Chl. a and relatively low dissolved organic matter. One explanation for these observations is that particulate matter from the estuary collects at the seaward edge of the plume and acts as a substrate for microbial activity that uses Mn-oxides to degrade humic material thus bringing about the release of dissolved Mn and promoting productivity. Murray (1985) reported a total dissolved Mn concentration in the Columbia River of 75nmol/kg. Finally, several authors, while not reporting data directly from the Columbia, have attributed elevated Mn signals to output from the river (and other rivers draining into this region). For example, Jones and Murray (1985) suggested that the surface maximum in waters in the northeast Pacific off Washington over the continental slope was due to fluvial input from the Columbia River and possibly from the Fraser and other small rivers draining Washington State. Landing and Bruland (1980, 1986) suggested that some of the high dissolved Mn concentrations observed in surface waters of several northeast Pacific stations (5-6nmol/kg, 1986; 10-12nmol/kg, 1980) were due to fluvial input.

#### 4.2.2 Aluminium

Rivers are a potential source of dissolved Al to the open ocean with the reported average dissolved Al concentration for world rivers being about  $1.85 \times 10^3$  nmol/l (Martin *et al*, 1991); however removal in estuaries and coastal waters is often so dramatic, particularly in highly productive coastal regions, that the importance of fluvial input as a source of dissolved Al the open ocean is extremely variable. Hydes and Liss (1977) and Sholkovitz (1976) suggest about 10-70% of "dissolved" Al supplied by rivers is lost to sediments as a result of salinity induced flocculation in estuaries. Orians and Bruland (1986) reported further removal in highly productive coastal regions of the Northeast Pacific due to scavenging on biogenic particles; Hydes (1989) suggested that low concentrations of Al in coastal waters of the Northeast Atlantic are maintained by

biologically mediated removal processes; and Mackin and Aller (1984) suggested that Al may be removed from estuaries via reaction with silicate and cations in solution. Maring and Duce (1987) and Moran and Moore (1988) suggested that the biogenic particle-removal rate of Al from coastal surface waters was comparable to the global estimate of fluvially derived Al inputs ( $9.66 \times 10^9 \text{ mol Al yr}^{-1}$ ) resulting in little fluvial input of Al into open ocean waters. Some authors, however, have observed elevated Al signals in low salinity waters and have attributed that elevation to fluvial sources: for example, Measures *et al* (1984) reported elevated Al signals (up to 75nmol/kg) coincident with low salinity surface waters of the Panama Basin; Upadhyay and Sen Gupta (1994) observed enrichment of Al (55-74nM) in low salinity waters ( $s=35.4$ ) off the Goa coast compared with lower levels of Al (37-52nM) in higher salinity ( $s>36$ ) waters off Bombay, and Upadhyay (1994) further suggested that only a small fraction of fluvially derived dissolved Al is removed in the Mandovi estuary; Kremling and Hydes (1988) reported elevated dissolved Al concentrations (about 28-48nmol/kg) in low salinity waters of the German Bight and the French coast; and El-Nady and Dowidar (1997) found, using a suite of samples from the Southeast Mediterranean, that Al concentrations were high in waters influenced by discharge from Lake Burullus ( $0.42 \mu\text{mol}$ ) and Lake Manzalah ( $0.19\text{-}0.31 \mu\text{mol}$ ).

#### 4.2.3 Cadmium

Table 4.2.3.1 shows concentrations of dissolved Cd in some world rivers. The world average dissolved concentration of Cd in rivers is estimated at 0.09nM (Martin and Windom, 1991) and ranges from 0.03nM in the Changjiang (Edmond *et al*, 1985; Elbax-Poullicher *et al*, 1987; Zhang, 1994) to 0.4nM in the Ebro (Guieu *et al*, 1991). The estuarine behavior of Cd is well documented, and shows a general tendency for release of Cd from particles in the estuarine environment (see for example Edmond *et al*, 1985; Boyle *et al*, 1982; Duinker *et al*, 1982; Salomons and Kerdijk, 1986). Cd concentrations typically increase to a maximum at low salinities (typically  $s<15$ ) in estuaries. The maximum has been attributed to a desorption from the particulate phase via formation of soluble Cd-chloro and Cd-sulphato complexes (see for example Duinker *et al*, 1982; Salomons and Kerdijk, 1986).

This type of behavior has been observed by many authors. For example, Shiller



and Boyle (1991) observed non-conservative behavior of Cd in the Mississippi River Delta with maximum concentrations of dissolved Cd (up to 300pM) occurring at salinities between 5-15; Boutier *et al* (1992) observed significant resolubilization of dissolved Cd in the Loire estuary (France) such that the input influence extended as far as western Brittany; and Harper (1990) observed values as high as 75-475nM in the lower salinity outer Severn estuary compared with 12-50nM in the higher salinity outer Bristol Channel. In general, in macrotidal estuaries such as the Amazon, the Changjiang, the Mississippi, the Seine and the Loire, the release of Cd from particles can multiply the input of dissolved Cd to the ocean by up to 30 times, whereas in stratified and microtidal estuaries such as the Rhone, the Lena and the Danube only small excesses in input are observed (Edmond *et al*, 1985). This may reflect either the short residence time of particles in such systems or the low particle content of these rivers.

**Table 4.2.3.1 Concentrations of Dissolved Cd in Some World Rivers**

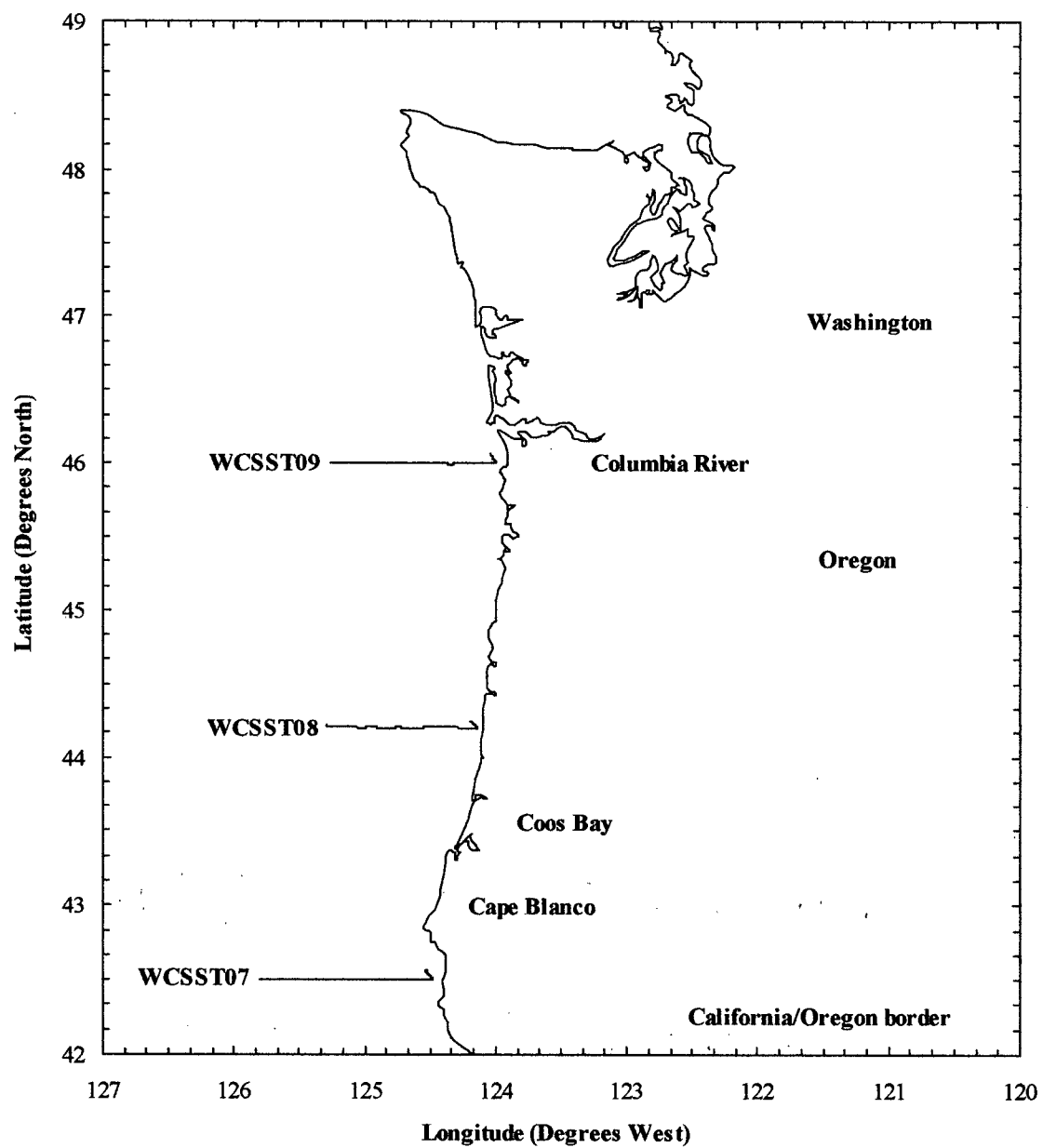
| <b>River</b>                                      | <b>Cd (nM)</b> |
|---|----------------|
| Changjiang (Edmond <i>et al</i> , 1985)           | 0.035          |
| Mississippi (Shiller, 1991)                       | 0.12           |
| Amazon (Boyle <i>et al</i> , 1982)                | 0.06           |
| Rhone (Boutier <i>et al</i> , 1992)               | 0.27           |
| Ebro (Guieu <i>et al</i> , 1991)                  | 0.4            |
| Huanghe<br>(Elbax-Poulicher <i>et al</i> , (1987) | 0.03           |
| Danube (Guieu <i>et al</i> , 1998)                | 0.12           |
| World average<br>(Martin <i>et al</i> , 1991)     | 0.09           |

#### **4.3 Study Area (figure 4.3.1)**

The Columbia River and estuarine system have been investigated thoroughly by several authors (Simenstad *et al*, 1984, 1991; Huyer, 1974, 1977). The river flows 2000km from southeastern British Columbia across Washington State before discharging into the Pacific Ocean. It is the second largest river in North America in terms of length

and volume and supplies 60% (winter) to 90% (summer) of the freshwater discharged into the Pacific Ocean between San Francisco Bay and the Strait of Juan de Fuca. Flow is significant, ranging from  $3,000\text{--}12,000\text{m}^3\text{s}^{-1}$  with a mean annual value of  $7,300\text{m}^3\text{s}^{-1}$ , and the annual discharge rate is  $2.5 \times 10^{11}\text{m}^3\text{yr}^{-1}$  (United States Geological Service data). Surface currents along the Washington, Oregon and California coastlines are primarily wind driven and fluctuate during the year (Simenstad *et al*, 1984). The river plume thus drifts north or south depending on the seasonal wind patterns. During winter, southerly winds dominate and coastal currents are northward; onshore Ekman transport of surface water and downwelling close to the coast are often observed, and the river plume is directed northwards along the Washington coastline. In late April/early May the jet stream alters position and northerly winds predominate; offshore Ekman transport results and upwelling occurs along the coast. The river plume is now directed along the Oregon coast. By late September/ early October winter conditions return.

Study periods for this research were late June/early July. During this period riverine discharge into the California Current system is limited to the Fraser River (which discharges into the Pacific via the Strait of Juan de Fuca at  $48^{\circ}30'\text{N}$ ) and the Columbia River (which discharges directly into the Pacific at  $46^{\circ}15'\text{N}$ ). Discharge from smaller Oregon and California rivers and various coastal streams is negligible (Huyer, 1983). Columbia River discharge is easily distinguishable from the surrounding coastal waters. Its salinity is very low when it reaches the sea ( $s \leq 21$ ). These low salinity waters are diffused both vertically and horizontally. They initially form a shallow lens overlying the California Current. The lens extends offshore and moves south and west as far as southern Oregon. Off central and northern Oregon the plume often lies sufficiently close to the shore that its inshore boundary overlaps with the offshore upwelled water boundary. Both temperature and salinity increase southward.



**Figure 4.3.1**

**Study area showing transects influenced by the Columbia River effluent.**

## 4.4 Results

### 4.4.1 Background California Current Trace Metal Values

Background California Current surface water values were determined for Mn (3-5nmol/kg), Al (0.38-0.65nmol/kg) and Cd (0.08-.46nmol/kg) (see Chapter 3, this work). These values reflect water that is not impacted by upwelling or riverine processes. This data agrees well with previous work. Mn values agree with Landing and Bruland (1980) who suggested values ranging from ~4-6nM in California Current waters off Santa Cruz and Jones and Murray (1985) who reported values ranging from ~4-8nM in waters off Washington. The Al data agrees with Orians and Bruland (1986) who determined Al values ranging from 0.3-1nmol/kg in California Current waters off Santa Cruz. Cd values agree with Bruland (1980) who reported values of 0.059-0.16nmol/kg for waters off Santa Cruz.

### 4.4.2 Physical data and nutrients (Figures 4.4.2.1-4.4.3)

Temperature, salinity and nutrient data indicate that transects WCSST09, WCSST08 and WCSST07 are strongly influenced by Columbia River input. The data effectively identify the position of the Columbia River plume. The primary core of the plume is characterized by low salinity ( $s=21-28$ ), low temperature ( $16-18^{\circ}\text{C}$ ), high silicate (silicate=10-40 $\mu\text{M}$ ) waters with lowest SST values ( $s=21$ ;  $t=16^{\circ}\text{C}$ ) coincident, as expected, with stations closest to the estuary at WCSST09. There appears to be evidence in this transect for a secondary core, similar in salinity, but warmer, and located further offshore than the primary core. In summer, outflow typically moves to the southwest under the influence of prevailing winds (Hickey, 1979; Barnes *et al*, 1972; Huyer, 1975). Physical and nutrient data confirm this and allow easy monitoring of the plume as it travels south and mixes with adjacent water masses. The plume retains its characteristic signal as far as WCSST07, more than 200km south of the head of the river.

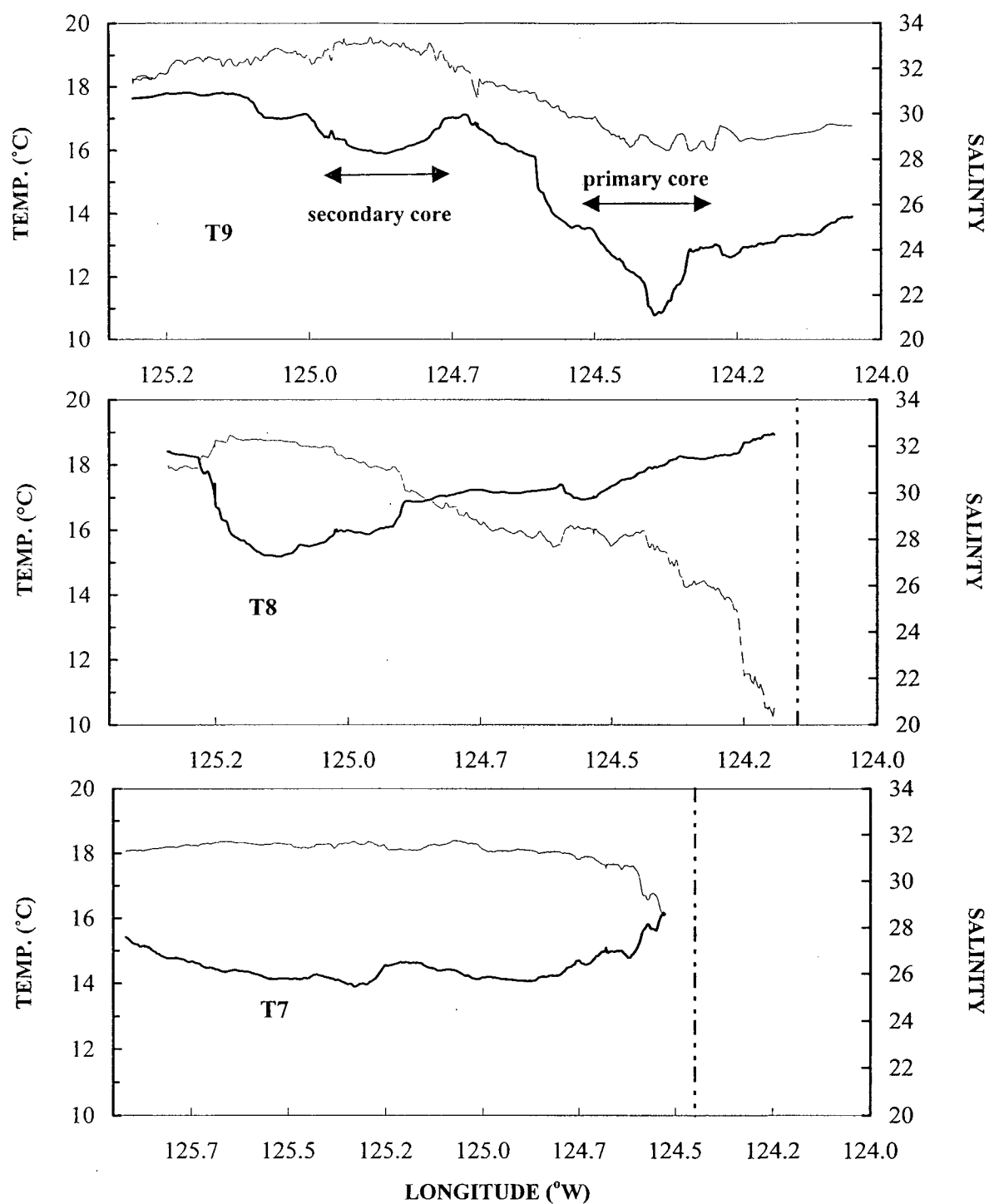
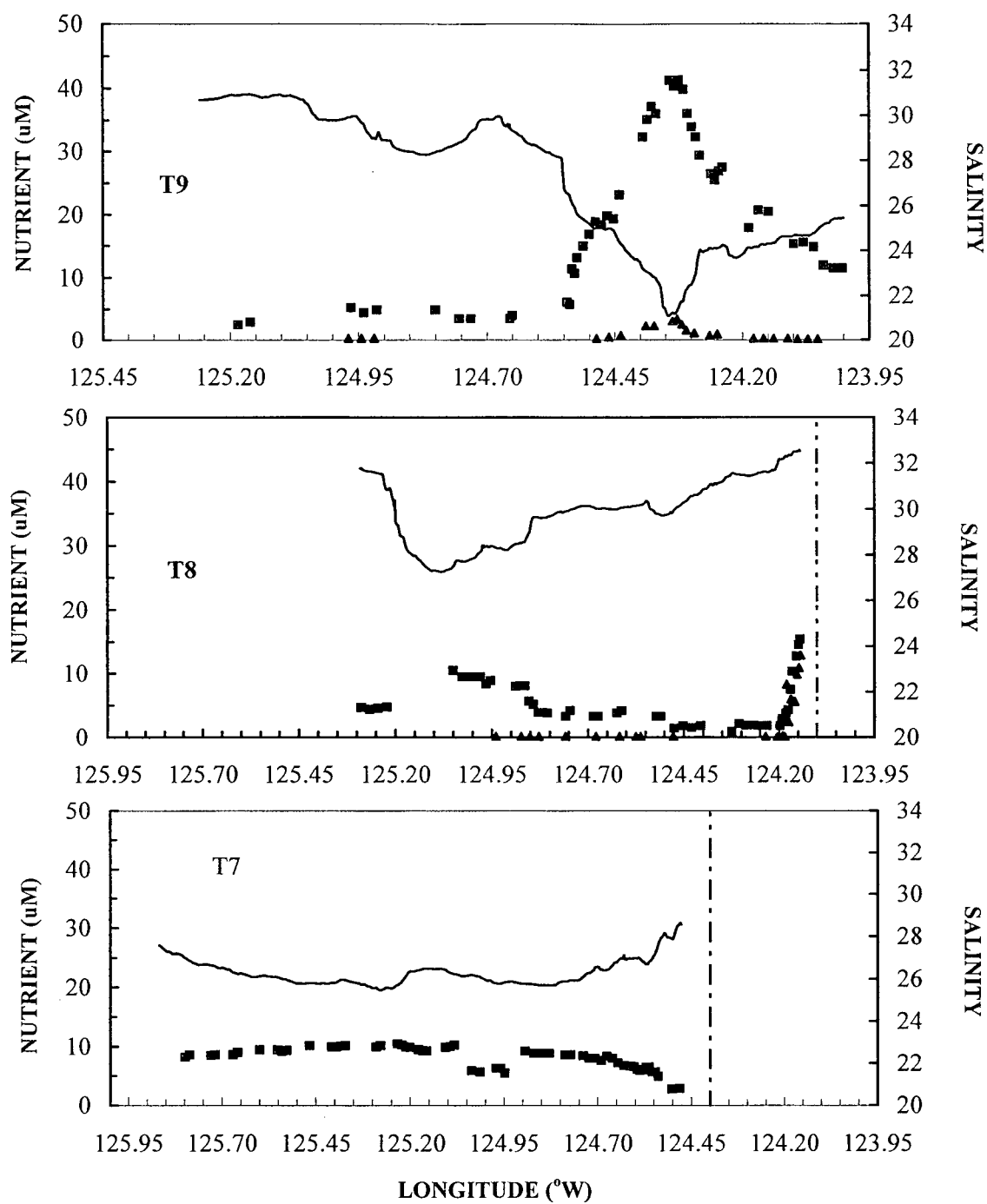


Figure 4.4.2.1

Temperature and salinity data for WCSST09, 08 and 07.

(Legend: solid line=salinity; broken line=temperature; dashed line=coastline)



**Figure 4.4.2.2**  
**Nutrient data for WCSST 09, WCSST08, WCSST07**

(Legend: ■=silicic acid; ▲=nitrate; solid line=salinity; dashed line=coastline)  
 (No flowthrough data available for nitrate at WCSST07)

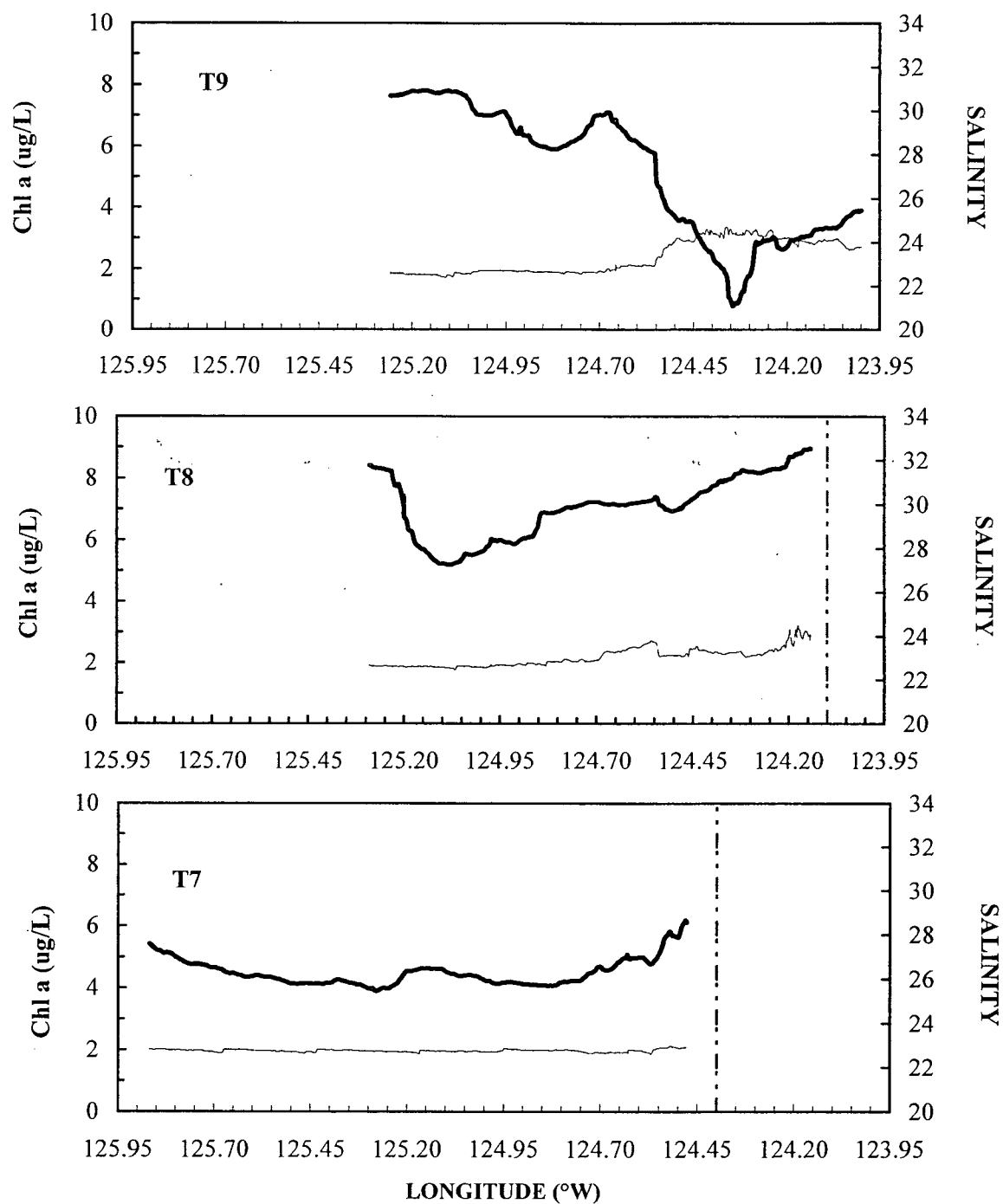


Figure 4.4.2.3

Chl a data for WCSST09, WCSST08, WCSST07

(Legend: broken line=Chl a; solid line=salinity; dashed line= coastline)

#### 4.4.3 Trace Metal Data (figures 4.4.3.1-4.4.3.4)

Ga data obtained by Lanthier (1999) will be referred to in this section as it provides an interesting complement to the Mn, Al and Cd data. Ga has a background value of 5-8pM in California Current surface waters.

Dissolved Mn, Al and Ga concentrations are highest in the lowest salinity waters of the Columbia River and decrease significantly as salinity increases. All metals are significantly elevated in the river plume (up to 117nmol/kg for Mn, 1.1nmol/kg for Al and 72pmol/kg for Ga at  $s=21$ ) above California Current background values (Mn=3-5nmol/kg; Al=0.38-0.65nmol/kg; Ga=5-8pmol/kg). Cd values are at background for all of the transects, except for one patch of upwelled water near the coast at WCSST08.

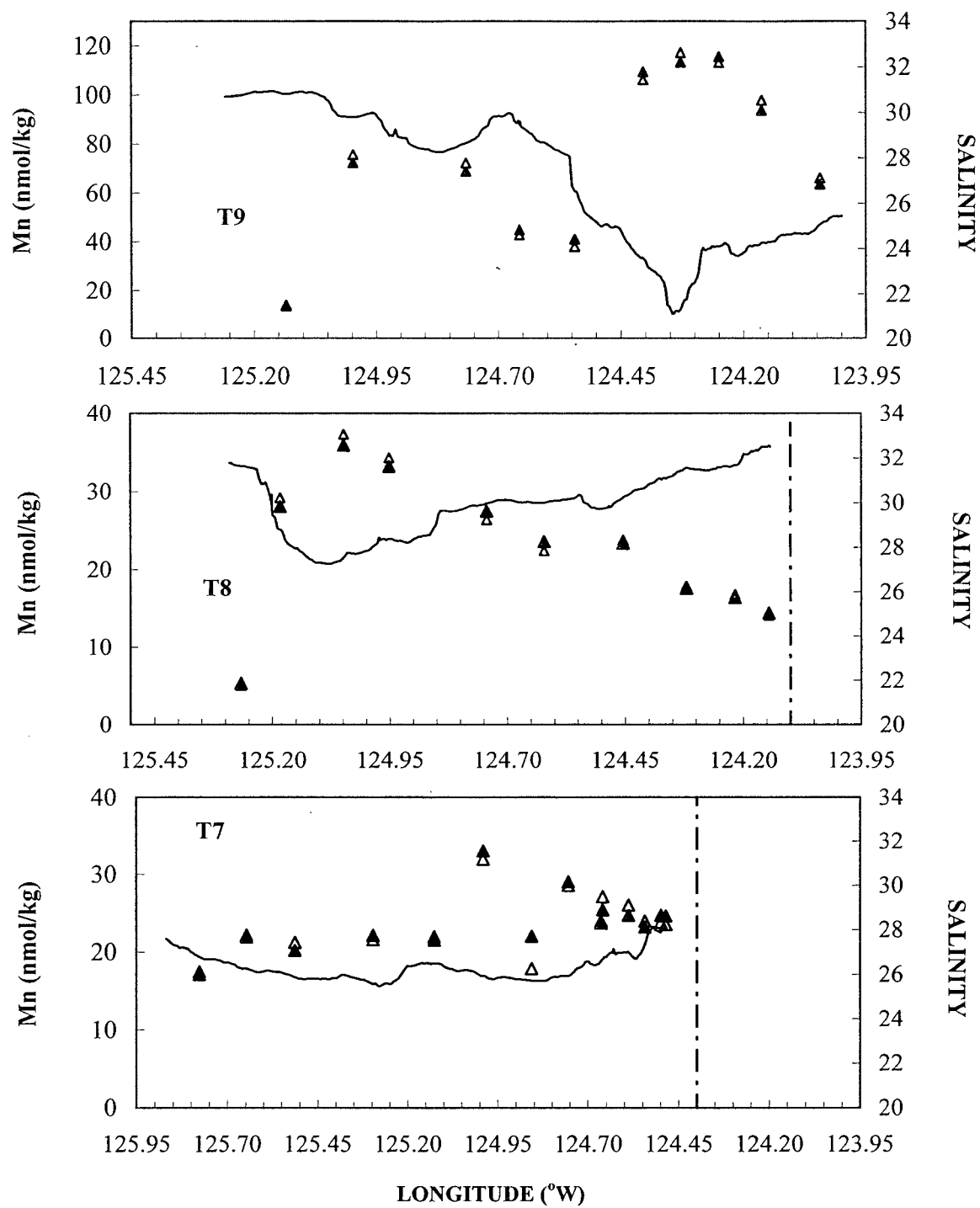
For Mn, concentration maxima are observed in the primary and secondary cores of WCSST09 (106-117nmol/kg and 69-76nmol/kg respectively) and concentration minima between the cores (38-43nmol/kg) and west of the secondary core (14nmol/kg). Concentrations remain elevated in the core at WCSST08 (28-37nmol/kg) and a significant decrease is again observed at the western end of the transect (5nmol/kg). At WCSST07 concentrations are fairly constant and elevated across the entire transect (17-33nmol/kg).

Al exhibits a concentration maximum coincident with the primary core of the plume at WCSST09 (1.0-1.1nmol/kg), concentrations then decrease rapidly to background. Unlike Mn no elevation is observed in the secondary core. Concentrations at WCSST08 and WCSST07 are uniform and at background across the entire transect.

Ga exhibits concentration maxima in the primary and secondary core of the plume at WCSST09 (49pmol/kg and 72pmol/kg respectively) and a lower concentration between the cores (16pmol/kg), at the western end of the transect (43pmol/kg) and closest to the coast (30pmol/kg). Concentrations remain elevated in the core at WCSST08 but are now approximately 50% lower in comparison to WCSST09. At WCSST07 Ga concentrations are fairly uniform across the transect (approximately 30pmol/kg) with a slight decrease observed toward the coast.

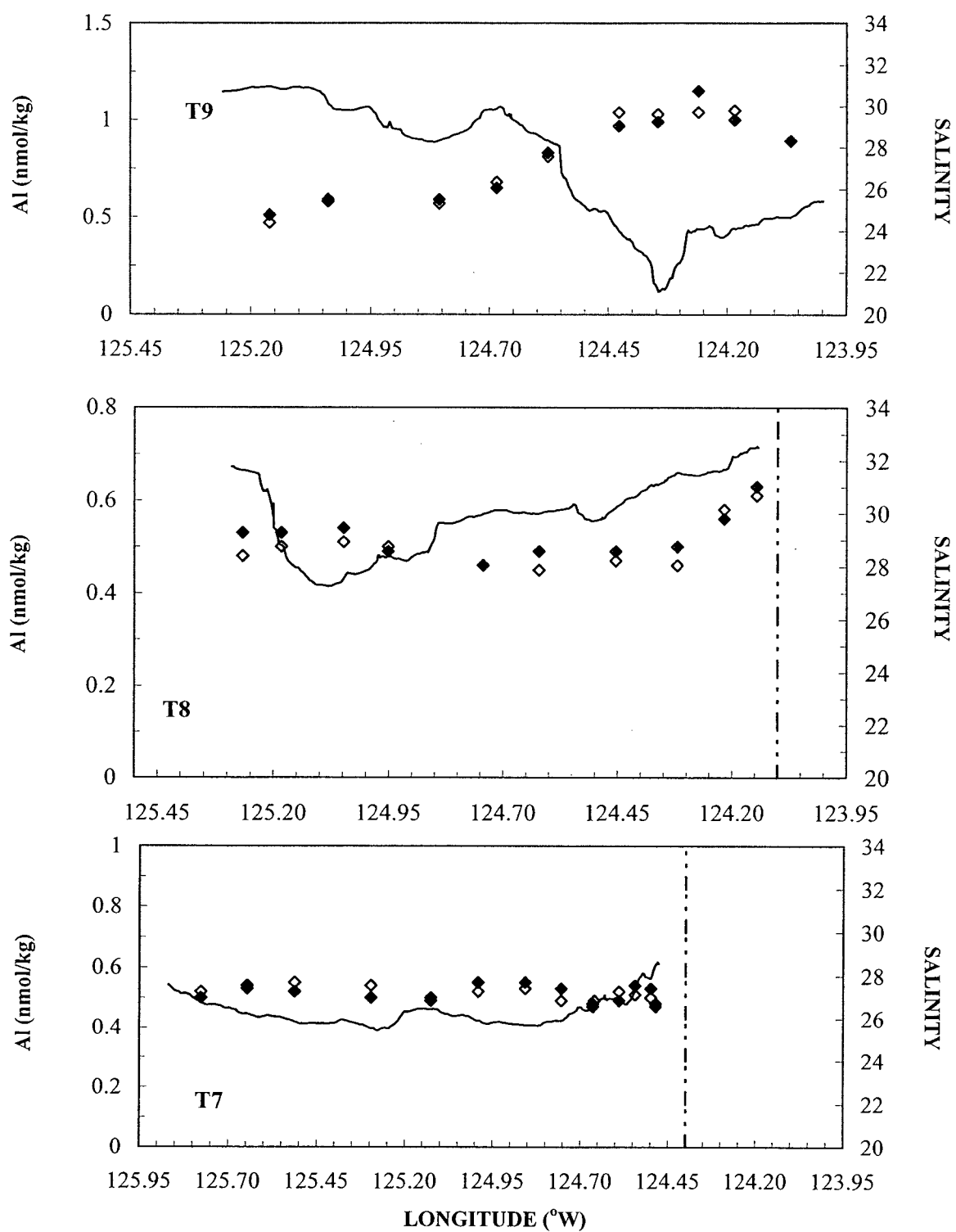
For Cd concentrations remain at background throughout transects WCSST07-09 (0.10-0.29nmol/kg). Concentrations are typically higher in the eastern sector of all transects (0.18-0.29nmol/kg) and then decline slowly to very low values (0.1-0.18nmol/kg)





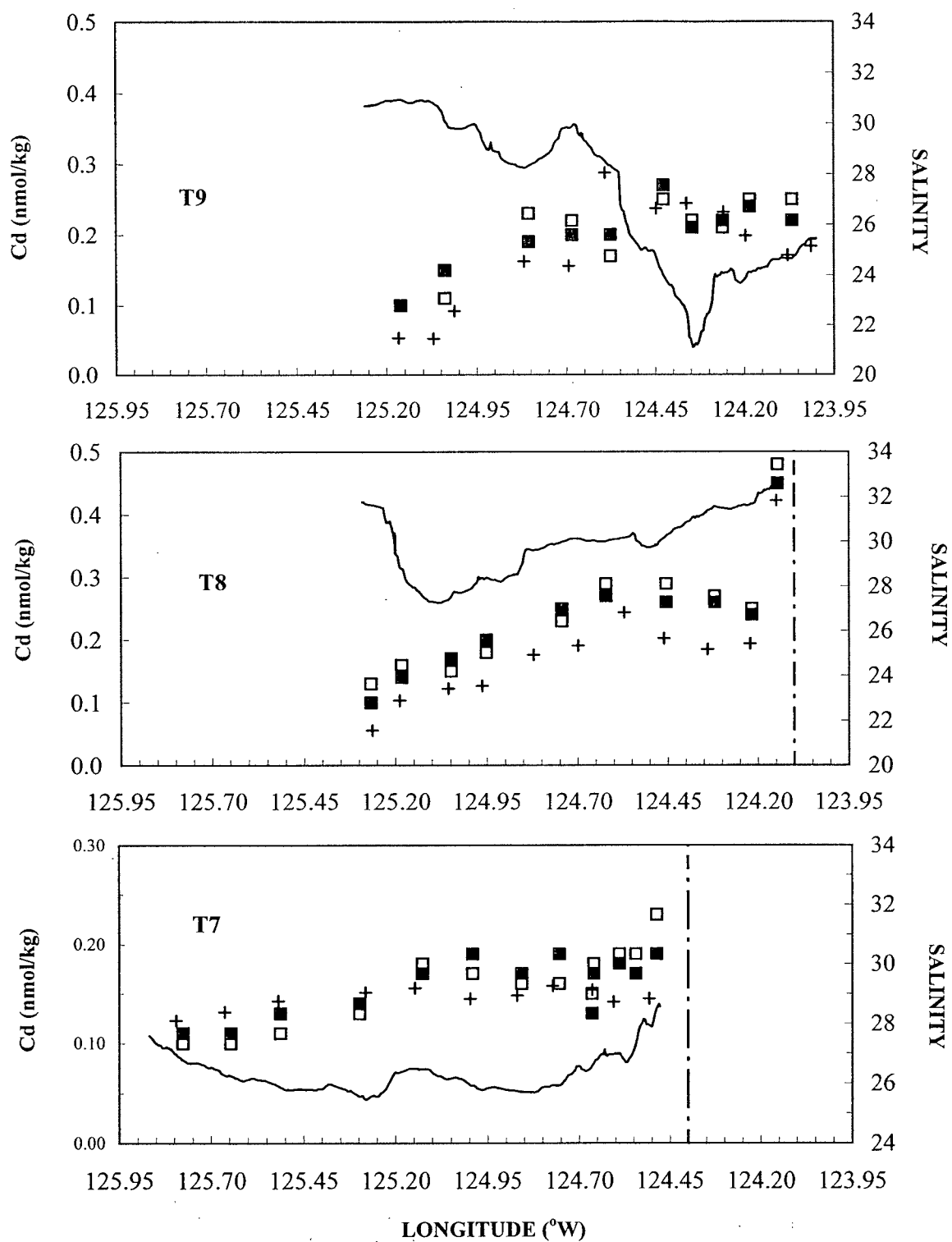
**Figure 4.4.3.1**  
**Mn data for WCSST09, WCSST08 and WCSST07**

(Legend: solid line = salinity; broken line = coastline;  
 open and closed ▲ = Mn replicates)



**Figure 4.4.3.2** Al data for WCSST09, WCSST 08 and WCSST 07

(Legend: solid line = salinity; dashed line = coastline; open and closed  $\diamond$  = Al replicates)



**Figure 4.4.3.3 Cd data for WCSST09, WCSST08 and WCSST07**  
**Legend:** solid line = salinity; broken line = coastline; ■ = Cd replicates;  
 + = Cd (UCSC data).

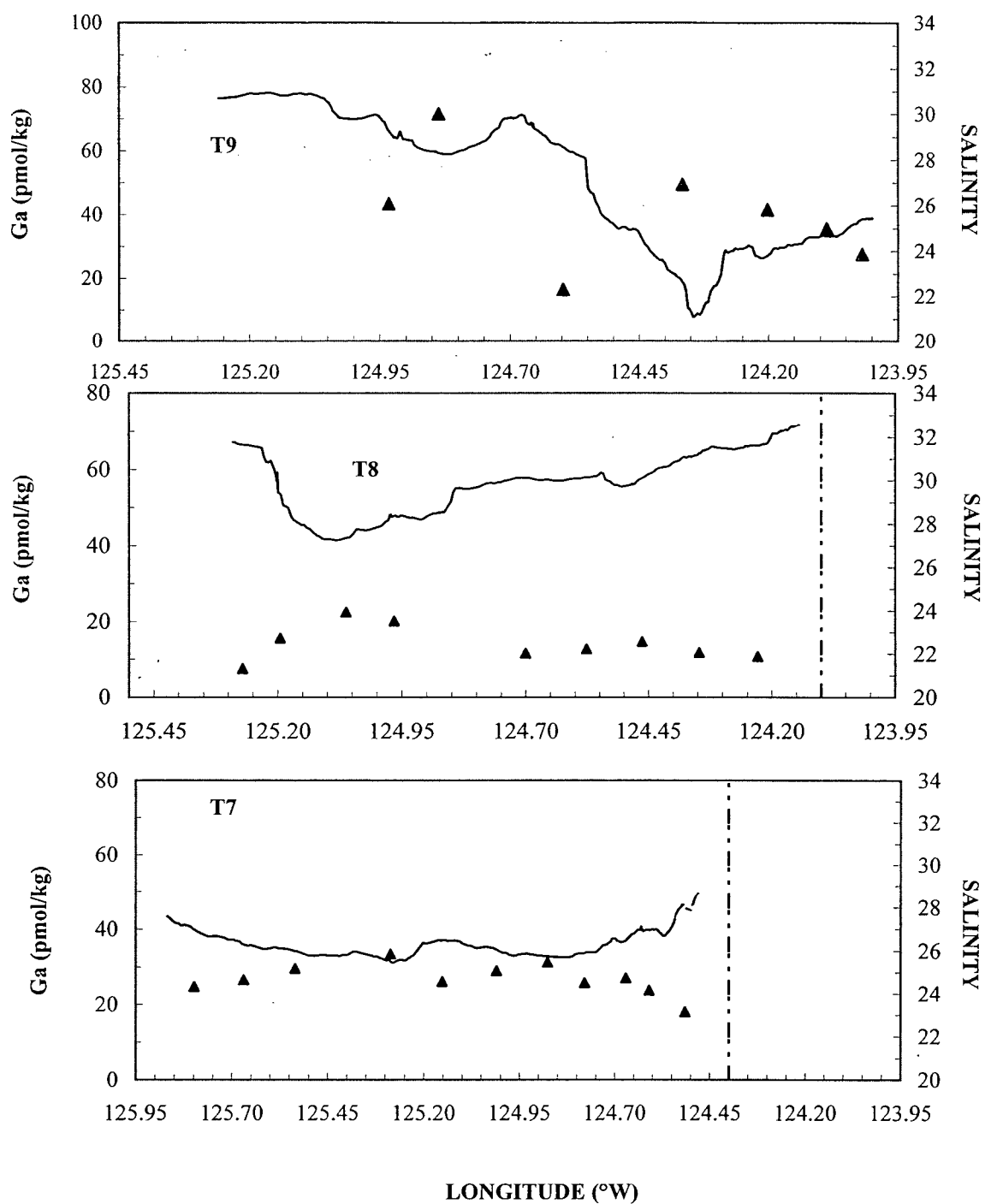


Figure 4.4.3.4

Ga data for WCSST09, WCSST08 and WCSST07

(Legend: solid line = salinity; vertical dashed line = coastline; ▲ = Ga)

## 4.5 Discussion

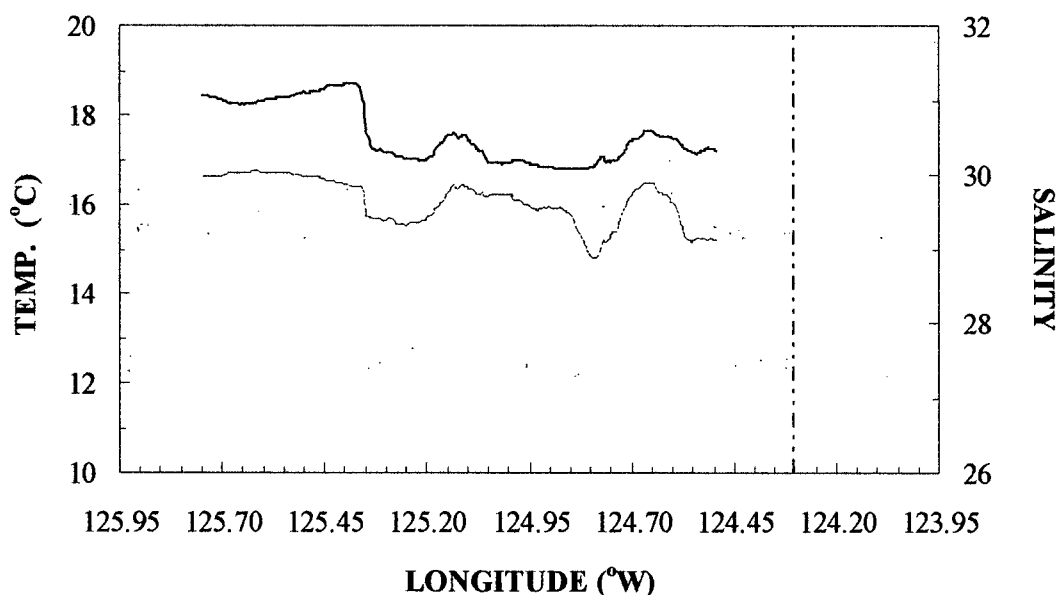
### 4.5.1 Physical and nutrient data

A number of interesting features are observed at Transects 7-9. At WCSST09 the primary core of the plume with a salinity of 21 and temperature of 21°C is observed close to the shore. Evidence exists for a secondary core with a salinity ( $s=28$ ) signature similar to that of the plume core at WCSST08 but warmer ( $t=19.5^{\circ}\text{C}$ ); this may be explained either via advection of a water mass from a northern location, however hydrographic data from WCSST10 does not support this (see figure 4.5.1.1), or more likely that this “secondary” core is a tongue of the plume that separated from the main body of the river, moved south and then back north, thus maintaining a low salinity and acquiring a higher temperature signal with time. Silicate data support the physical data well. High silicate signals (up to  $40\mu\text{M}$ ) are observed coincident with the primary core. Silicate data in the secondary core are unfortunately somewhat limited. On either side of the salinity minimum the silicate values do seem to rise slightly suggesting the secondary core is possibly an older water mass that has been subject to biological activity over time. Nitrate shows slightly elevated values (up to  $3\mu\text{M}$ ) only in the lowest salinity waters. Chl *a* data indicates a bloom is occurring in the primary core. There is no evidence of a bloom in the secondary core, or indeed at any other location and this is likely due to nitrate limitation.

At WCSST08 the primary core under the influence of prevailing winds is further offshore and salinity has increased to  $s=27-28$ . A relatively cool ( $10^{\circ}\text{C}$ ) and saline ( $s>32$ ) patch of recently upwelled shelf water is observed close to the shore. Both nitrate and silicate show the expected elevation coincident with this upwelling regime. Silicate continues to show elevation (up to  $10\mu\text{M}$ ; though considerably lower than that seen at WCSST09) coincident with the primary core of the plume.

The salinity signal is fairly constant at WCSST07; salinity has increased significantly ( $s=25-28$ ) but remains lower than typical California Current background water salinities ( $s>32.5$ ); and silicate has decreased ( $8-10\mu\text{M}$ ). It is interesting to note that salinity values here are slightly lower than for WCSST08 giving the impression that the plume is fresher. There are a number of possible explanations for this: local rivers in this area such as the Umpqua and Rogue may be discharging enough fresh water to influence the salinity significantly. However, numerous studies (see for example Huyer,

1977, 1979, 1983) have suggested that summer time discharge of Oregon rivers is essentially negligible. In addition, streamflow data (Rogue River -- June 1997: 4102ft<sup>3</sup>/s; July 1997: 2883ft<sup>3</sup>/s; Umpqua River -- June 1997: 3015 ft<sup>3</sup>/s; July 1997: 1980 ft<sup>3</sup>/s; Columbia River – June 1997: 550,500ft<sup>3</sup>/s; July 1997: 280,000ft<sup>3</sup>/s) from the United States Geological Service indicate that discharge was minor for these rivers during the time period of the study. Local storm and/or mixing events may cause extensive mixing of WCSST08 surface waters with underlying, higher salinity waters; however CTD profiles do not support this theory either. Both transects have a similar mixed layer depth of between 6-10m so presumably mixing is occurring at the same depth for WCSST07 and WCSST08. Finally, it is possible that some kind of advective feature or variability in Columbia River outflow with time could account for this anomaly.



**Figure 4.5.1.1**

**Temperature and salinity data for WCSST10**

**(Legend: solid line=salinity; broken line=temperature; dashed line=coastline)**

#### 4.5.2 Trace metal data

Data for Mn, Al and Ga strongly suggest that all three metals are supplied by the Columbia River. Both Ga and Mn show significant elevation above background in the primary core of the plume at WCSST09 (49pmol/kg and 106-117nmol/kg respectively). Ga shows greater elevation in the secondary core (72pmol/kg) whereas Mn shows a decrease from the primary value (69-76nmol/kg). Signals for both metals remain elevated as far south as WCSST07 rendering them useful tracers of the Columbia River plume. The signals continually decrease as the plume moves south from WCSST09 to WCSST07. This may suggest on-going removal, or may result from mixing with water containing lower concentrations of these constituents. Al shows elevation only in the primary core, signals then decrease more rapidly and to a greater extent than either Mn or Ga. Concentrations at WCSST08 and WCSST07 are constant and at background, thus Al is not as useful as a tracer of the Columbia as Ga or Mn. Cd does not appear to show any significant elevation above background in any of the transects (except where upwelling was seen along the coast at WCSST08) and thus is also not a useful tracer of the Columbia River.

In order to elaborate further on the chemical behavior and reactivity of Mn, Al, Ga and Cd, constituent-salinity diagrams were constructed. The constituent of interest (silicate, Mn, Al, Ga and Cd) is plotted against a property, such as salinity, that is known to act in a chemically conservative manner. The conservative property gives an indication of the dilution of freshwater by ocean water. If one now assumes that there are only two end-members (river water and seawater) in this system, that the system is one-dimensional, and further assumes that the system is at steady state (i.e. it does not show temporal variations in fluvial concentration), any curvature in the resulting constituent-salinity plot will indicate constituent chemical reactivity in the estuary. Conversely, a linear constituent plot indicates conservative (non-reactive) behavior by the constituent. This model has been used successfully by many authors (see for example Shiller, 1997; Shiller and Boyle, 1991; van Geen and Luoma, 1991; Flegal *et al*, 1991; Boyle *et al*, 1974) and has come to be regarded as a staple tool in the interpretation of estuarine nutrient and trace metal behavior (Kaul and Froelich, 1984). Figures 4.5.2.1 and 4.5.2.2 show the results of this model when applied to dissolved Cu and Cd in the outflow of the Mississippi (Shiller and Boyle, 1991). Figure 4.5.2.1 shows a conservative distribution;

presumably Cu is unreactive on the timescale of the dilution process. Figure 4.5.2.2, in contrast, shows Cd behaving in a non-conservative manner; here, presumably, Cd is desorbing from fluvial derived particles resulting in the maximum seen in the low salinity portion of the plot. Further information may be obtained from these types of plot by following the approach of Boyle *et al* (1974). This author suggested that extrapolation of the conservative mixing line back to zero salinity would give an estimate of original fluvial concentrations, while extrapolation of the tangent of constituent concentrations at high salinities would give an indication of effective fluvial input.

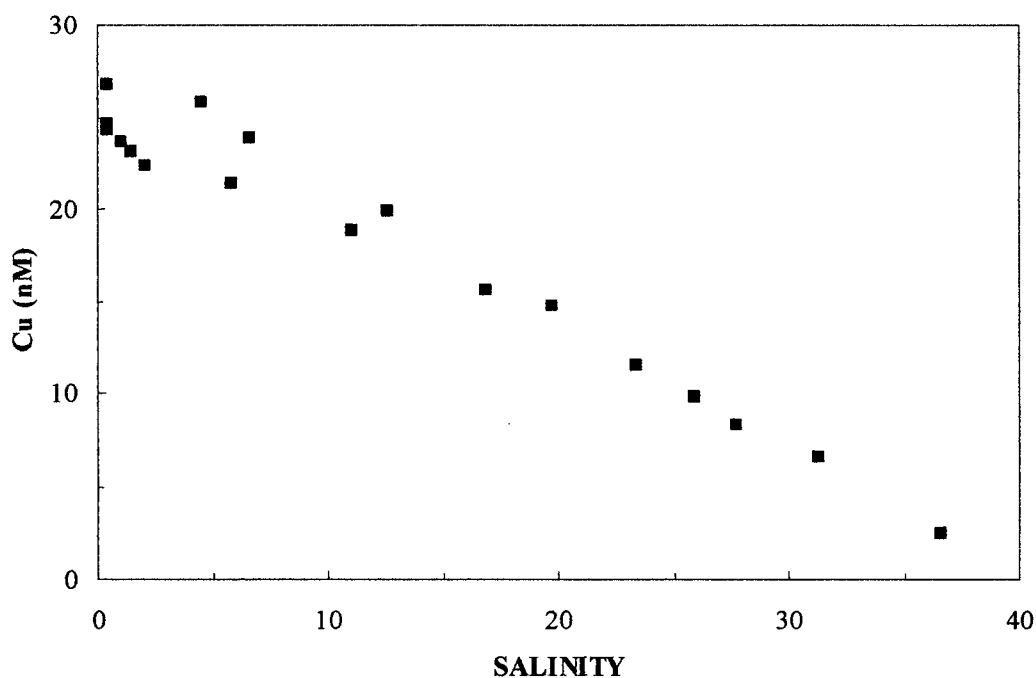


Figure 4.5.2.1      Dissolved Cu in the outflow from Southwest Pass, Mississippi River delta plume.  
(Shiller and Boyle, 1991)



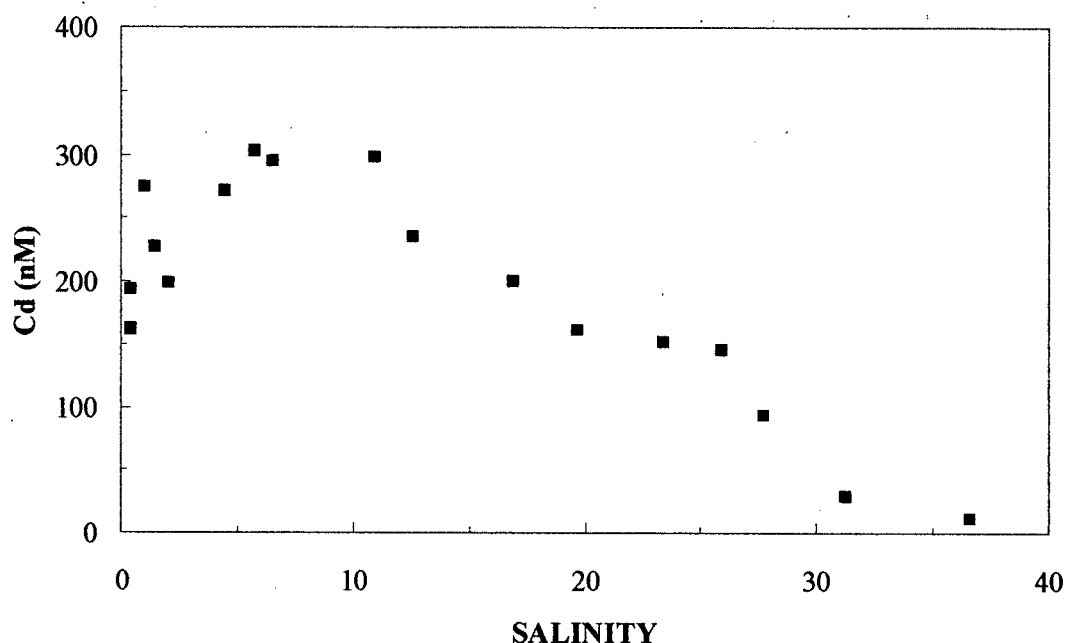


Figure 4.5.2.2 Dissolved Cd in the outflow from Southwest Pass, Mississippi River delta plume.  
(Shiller and Boyle, 1991)

The widespread, and seemingly ready use of these mixing plots unfortunately however, may lead to the neglect of some or all of the key assumptions and conditions that underpin the model. This may then result in incorrect statements being made regarding estuarine behavior. For example, Officer and Lynch (1981) pointed out that temporal variations in fluvial concentrations can result in curved constituent-salinity plots. The curvature would likely be incorrectly attributed to non-conservative behavior of the constituent, when in fact it was behaving conservatively. More recently, van Geen and Luoma (1993) realized that extrapolations of their nutrient-salinity and trace metal-salinity plots from the San Francisco back to zero salinity resulted in significantly higher concentrations than actual fluvial concentrations. In this case, a third end-member, upwelling, had violated the 2 end-member requirement of the model.

For this study of the Columbia River, a number of issues must be addressed before assigning significance to the constituent-salinity plots shown in figures 4.5.2.3-4.5.2.xx.

The region of coastline impacted by the Columbia River is probably influenced by

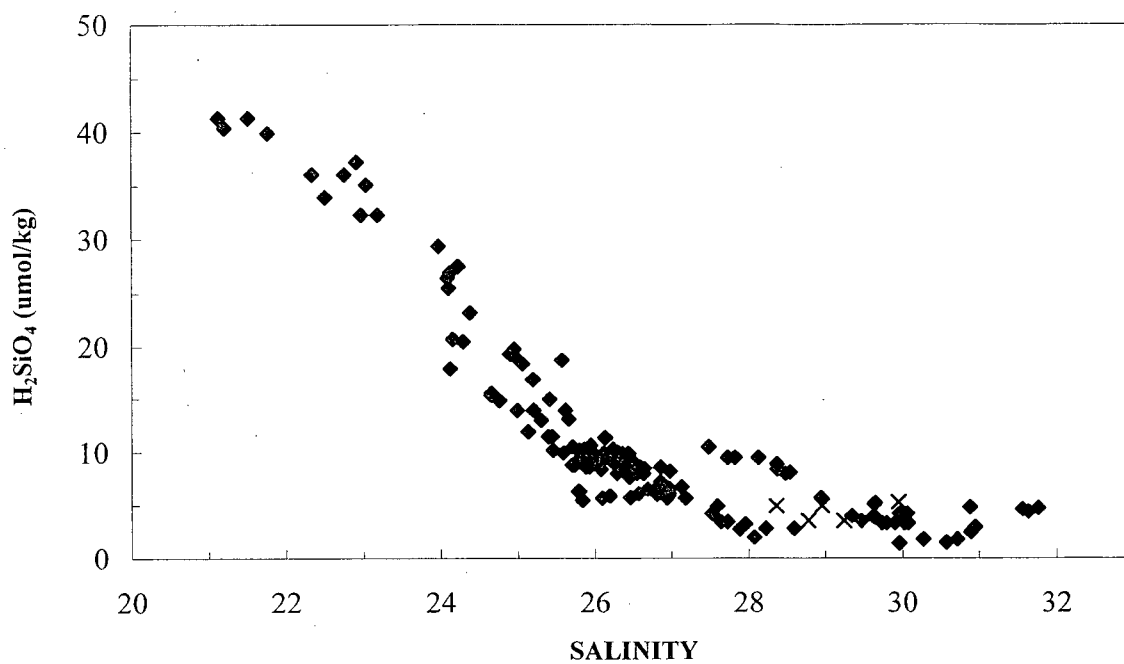
upwelling of metal and nutrient enriched deep waters to the surface. This will violate both the one-dimension and two end-member assumptions. This type of problem has been described by several authors including Shiller (1997), van Geen *et al* (1991) and Edmond (1981) and has led to the development of the idea of estuarine recycling traps. These traps occur when primary productivity in relatively low salinity surface waters converts dissolved material into the particulate state. The particulate material sinks to more saline, deeper waters and is recycled via oxidation back to the dissolved state. Eventually, gravitational circulation and/or upwelling transport enriched saline waters to the surface where they mix with fresh water. Van Geen *et al* (1991) used the recycling model to account for unusually high trace metal concentrations observed off the Gulf of Cadiz and Spain and Flegal *et al* (1991) to account for anomalously high metal signals in the San Francisco Bay. For this study of the Columbia River region, one of the most obvious violators of the one-dimensional, 2 end-member approach is the patch of cool, saline upwelled water observed just off the coast at WCSST08, and data from this area must certainly be excluded from any constituent-salinity analysis.

The second issue to be addressed in the Columbia River region is that of temporal variability. Variations in fluvial concentrations over the time scale of dilution can result in curved constituent/salinity plots when behavior is in fact conservative; thus any temporal variation of constituent end members (river and ocean) must be longer than estuary flushing time (the time required for river flow to replace the existing fresh water in the estuary) in order for the standard model to be valid. In other words, if fluvial concentration varies quickly relative to the estuary flushing time, there will essentially be several different types of river water mixing with the ocean end-member, which will result in apparent non-conservative behavior. Thus, an estimate of the timescale of mixing of both the estuary and the plume waters is essential to help with interpretation of data arising from this system. Klinkhammer (1997) recently suggested that the timescale of plume and estuary mixing is on the order of months. It is thus more than plausible that fluvial variation will occur more quickly. Indeed, if we do attribute the fresher water at WCSST07 compared with that at WCSST08 to temporal variation and further assume that this variation has taken place over a time scale of less than a month, then the simple steady state model will be violated. Another potential problem that may be addressed under this heading is that eddies or jets of river water may mix out to different salinities,

and then return to their original location with a different time history.

The final issue is that of the salinity range measured for this study. In this case, a relatively limited range of salinities was used to characterize the entire river-ocean mixing regime. While river water concentrations based on equally limited salinity ranges ( $s=30-35$ ) have been estimated by other authors (Boyle *et al*, 1984); in these cases the metal/salinity relationship was conservative which allows greater confidence to be placed on extrapolation of such limited data ranges. For this research, not only was the salinity range somewhat limited, but silicic acid, Mn, Al and Cd all potentially exhibited non-conservative behavior. It is very likely that some, if not all, of the metals investigated in this study behaved non-conservatively at salinities lower than were sampled. For example, it is well known that Cd typically exhibits a concentration maximum at low salinities, yet this maximum is not observed for the Columbia River, and one very plausible explanation is that the maximum occurred at salinities lower than were measured. Any extrapolation based on this data is thus likely to be somewhat tenuous. A similar argument can also be made for Al; this metal is very particle reactive in estuaries and significant quantities of dissolved Al are probably removed to the particulate phase through flocculation and/or scavenging in low salinity reaches of the estuary. If this removal takes place at salinities lower than I sampled, any estimates based on extrapolation will be underestimates.

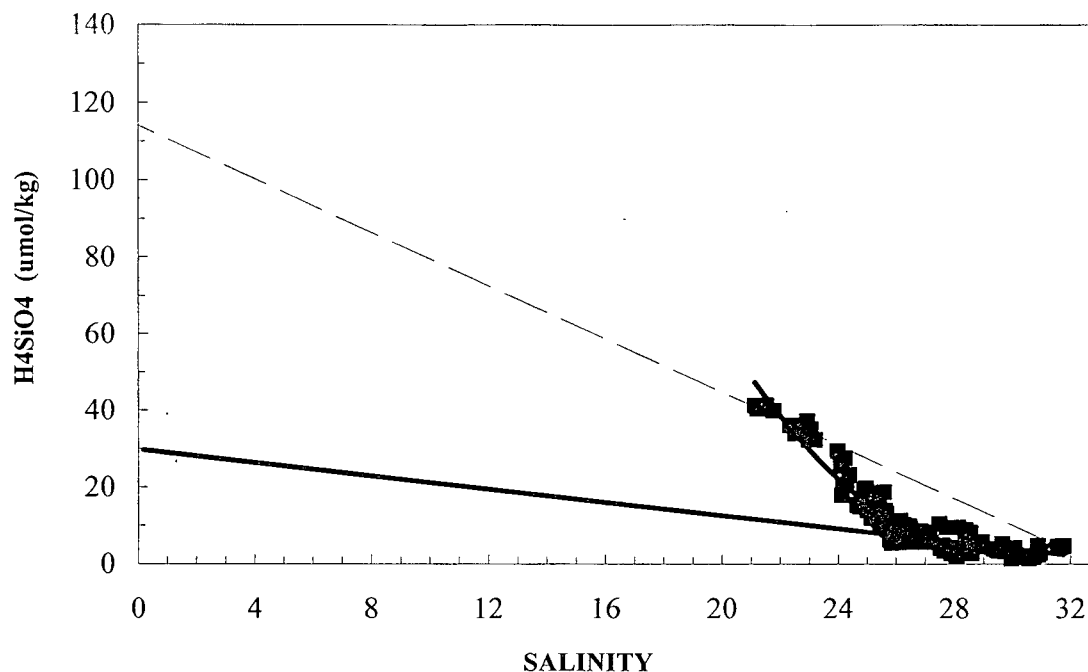
Despite these inherent difficulties, many authors have successfully used constituent-salinity plots to describe estuarine behavior (see for example Flegal *et al*, 1991; Edmond *et al*, 1981), and these plots may certainly be used for this study provided one realizes the limits of model in this area.



**Figure 4.5.2.3**

Silicic acid vs. salinity plot for transects WCSST07, WCSST08 and WCSST09

"X" represents secondary plume data. Data from the upwelling region near shore at WCSST08 have been excluded.



**Figure 4.5.2.4**

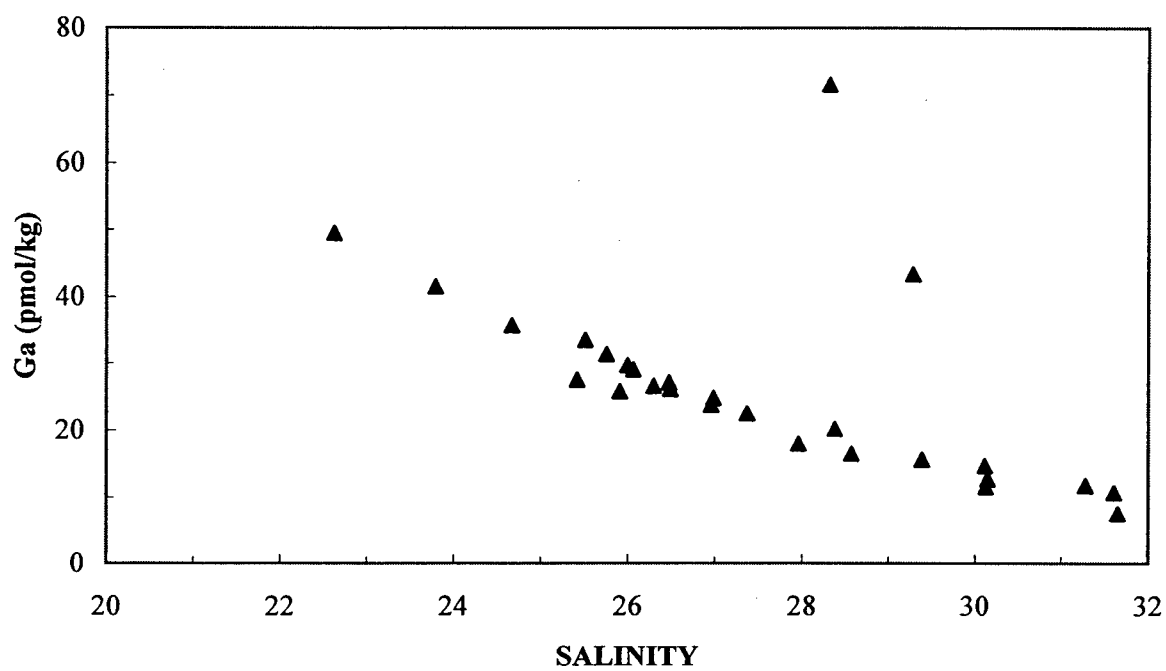
**Silicic acid vs salinity plot for transects WCSST07, WCSST08 and WCSST09.**

The original river concentration is obtained from extrapolation of the conservative mixing line back to back to zero salinity.

The conservative mixing line (dashed line) is obtained by a simple linear regression between river ( $s < 24$ ) and ocean ( $s > 31$ ) end-members.

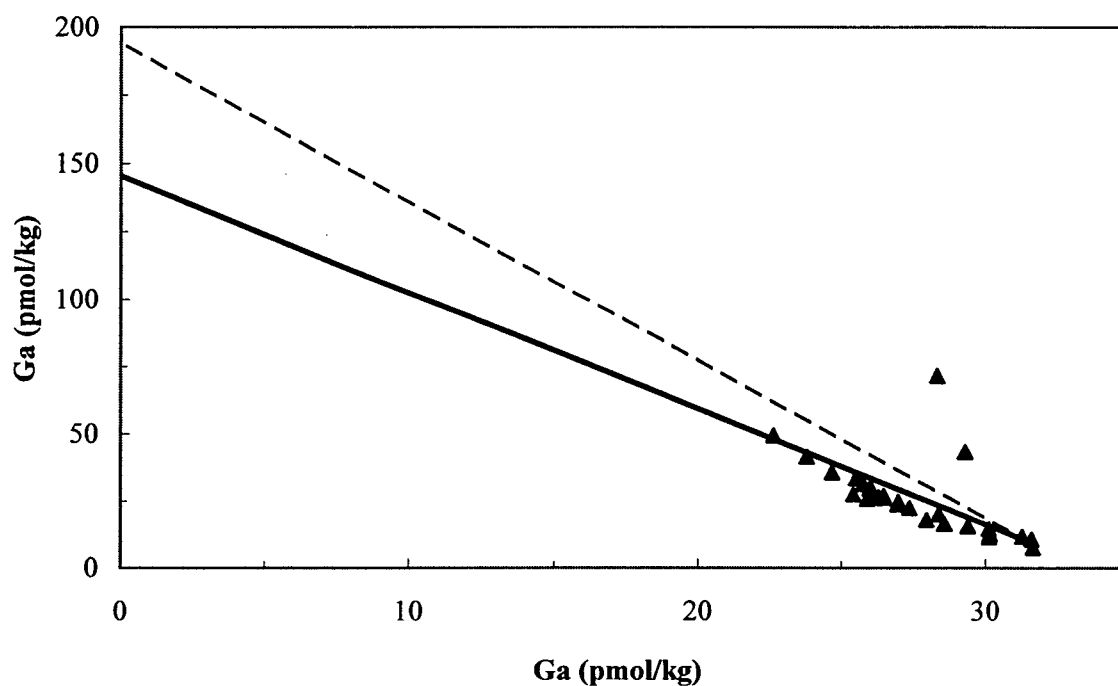
The effective river concentration is obtained from the intersection at zero salinity of the tangent of the metal (solid line) concentrations at high salinities, which reciprocally is obtained by linear regression of all the data of salinities above 27.

The curved line is a second order polynomial best fit ( $R^2=0.9121$ ) of all data except those from the secondary plume (not shown).



**Figure 4.5.2.5**

**Ga vs. salinity plot for transects WCSST07, WCSST08 and WCSST09.**



**Figure 4.5.2.6**

**Ga vs. salinity plot for transects WCSST07, WCSST08 and WCSST09.**

The original river concentration is obtained from extrapolation of the conservative mixing line back to zero salinity.

The conservative mixing line (dashed line) is obtained by a simple linear regression between river ( $s < 24$ ) and ocean ( $s > 31$ ) end-members.

The effective river concentration is obtained from the intersection at zero salinity of the tangent of the metal (solid line) concentrations at high salinities, which reciprocally is obtained by linear regression of all the data of  $s > 27$ .

The curved line is a second order polynomial best fit ( $R^2 = 0.6592$ ) of all data except those from the secondary plume (not shown).

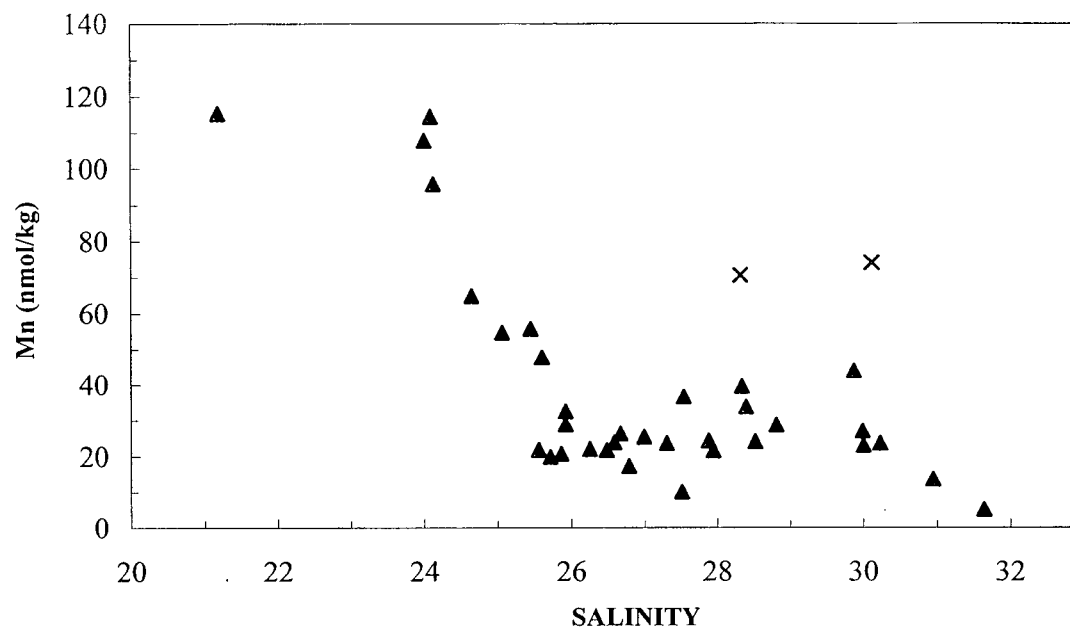
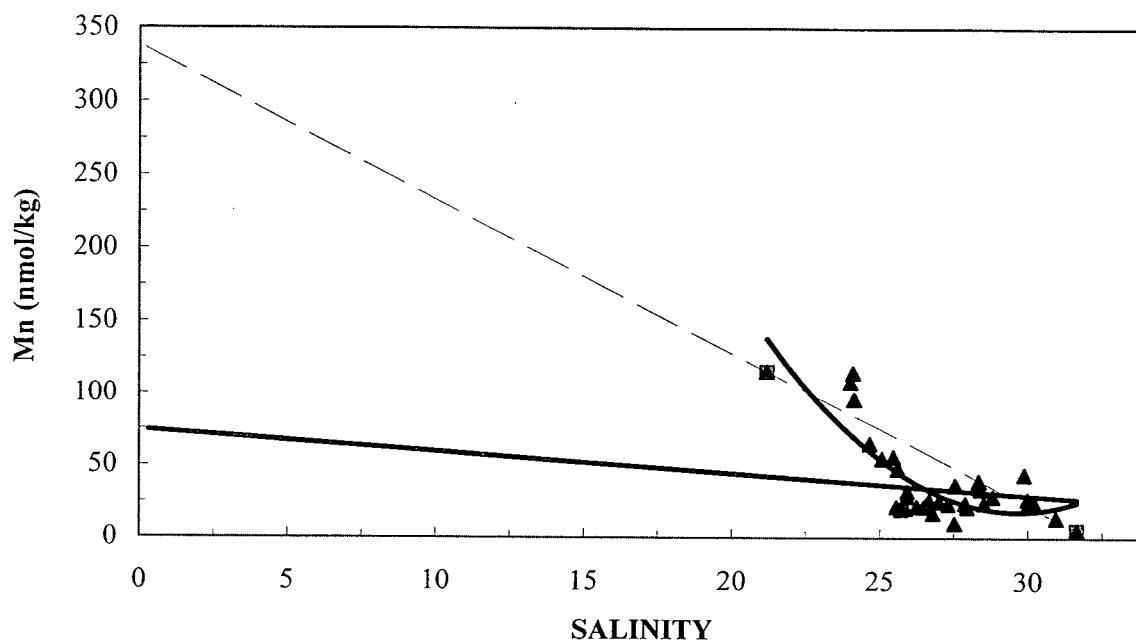


Figure 4.5.2.7

Mn vs. salinity plot for transects WCSST07, WCSST08 and WCSST09.

"X" represents secondary plume data. Data from the upwelling region near shore at WCSST08 have been excluded.





**Figure 4.5.2.8**

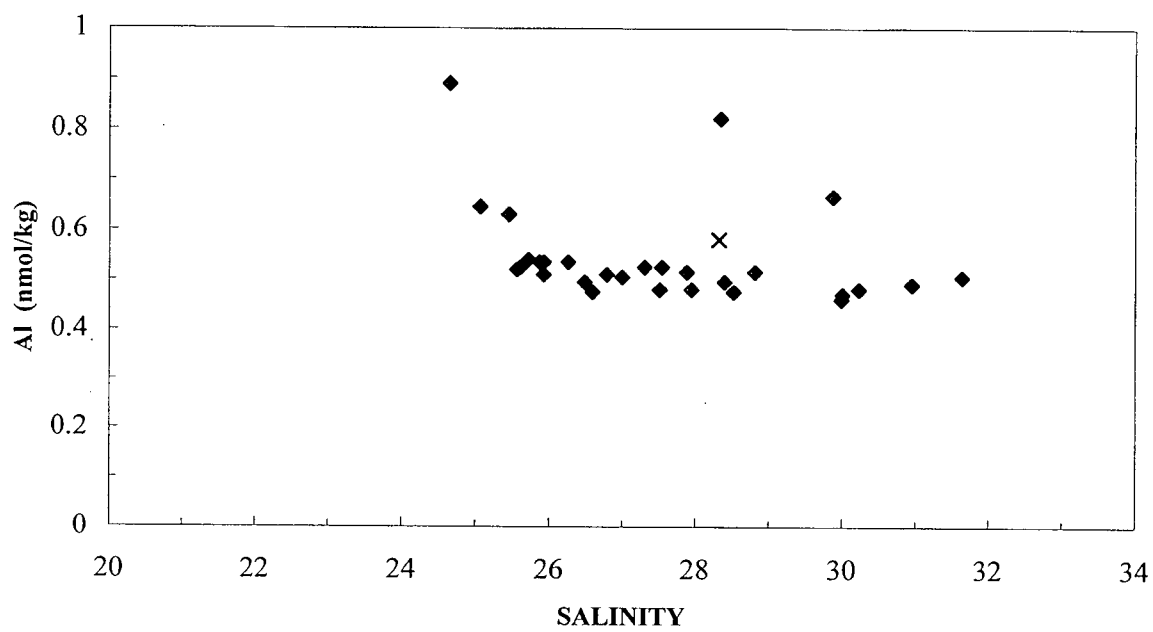
**Mn vs. salinity plot for transects WCSST07, WCSST08 and WCSST09.**

The original river concentration is obtained from extrapolation of the conservative mixing line back to zero salinity.

The conservative mixing line (dashed line) is obtained by a simple linear regression between river ( $s < 24$ ) and ocean ( $s > 31$ ) end-members.

The effective river concentration is obtained from the intersection at zero salinity of the tangent of the metal (solid line) concentrations at high salinities, which reciprocally is obtained by linear regression of all the data of  $s > 27$ .

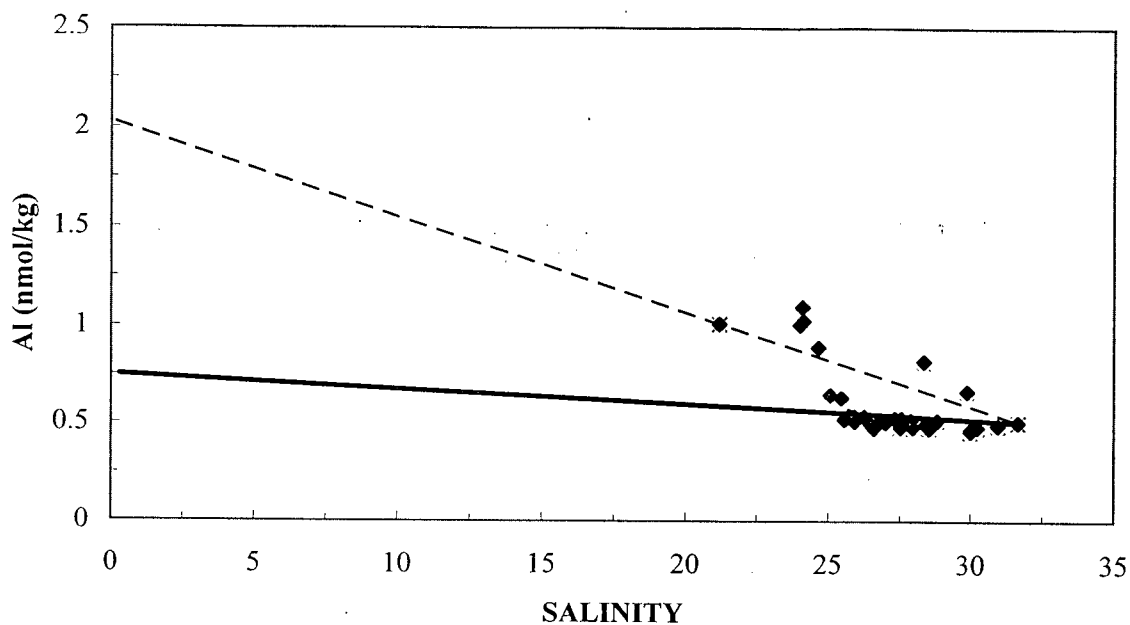
The curved line is a second order polynomial best fit ( $R^2 = 0.6592$ ) of all data except those from the secondary plume (not shown).



**Figure 4.5.2.9**

Al vs. salinity plot for transects WCSST07, WCSST08 and WCSST09.

"X" represents secondary plume data. Data from the upwelling region near shore at WCSST08 have been excluded.

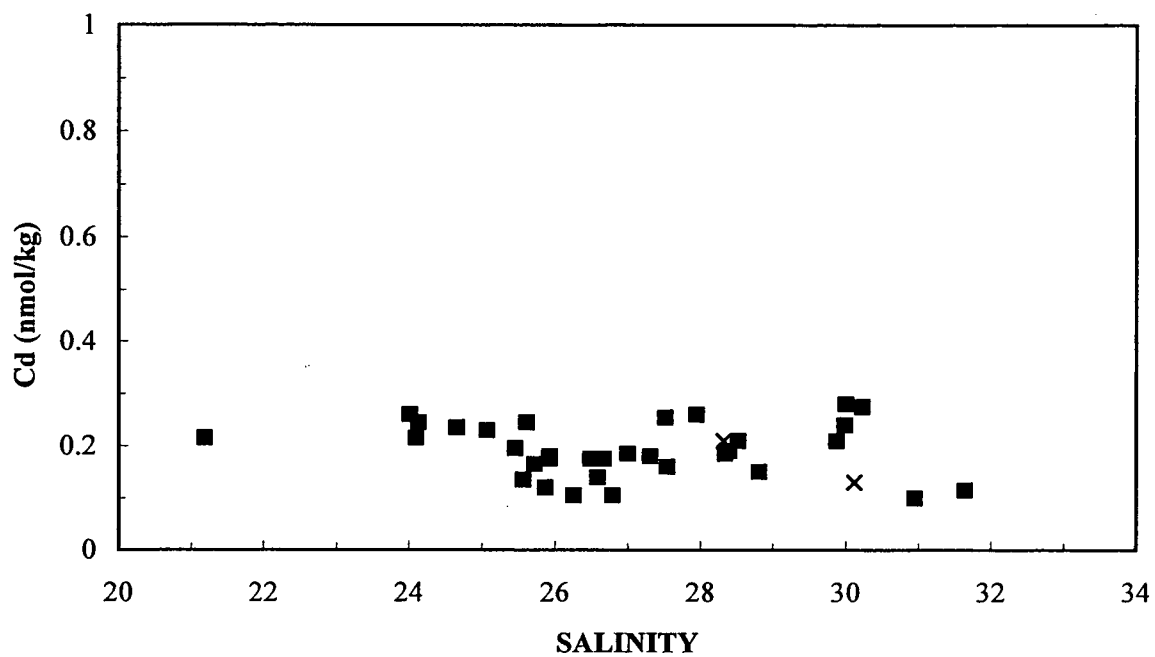


**Figure 4.5.2.10** Al vs. salinity plot for transects WCSST07, 08 and 09.

The original river concentration is obtained from extrapolation of the conservative mixing line back to zero salinity.

The conservative mixing line (dashed line) is obtained by a simple linear regression between river ( $s < 24$ ) and ocean ( $s > 31$ ) end-members.

The effective river concentration is obtained from the intersection at zero salinity of the tangent of the metal (solid line) concentrations at high salinities, which reciprocally is obtained by linear regression of all the data of  $s > 27$ .



**Figure 4.5.2.11**

Cd vs. salinity plot for transects WCSST07, WCSST08 and WCSST09

"X" represents secondary plume data. Data from the upwelling region near shore at WCSST08 have been excluded.

#### 4.5.3 Silicic acid

Dissolved silicic acid data shown in figures 4.5.2.1 and 4.5.2.2 are most simply interpreted as representing two distinct mixing regimes with very slow removal observed between  $s=21-24$  and significantly more rapid removal observed between  $s=24-31$ . This initial slow removal indicates a period of low biological activity. Waters in this region were very muddy, possibly leading to a decrease in light penetration and thus an inhibition of silicic acid uptake by phytoplankton. Conservative mixing has been observed for silicic acid in many estuaries (see for example Schiller and Boyle, 1991; Flegal *et al*, 1991; Boyle *et al*, 1974). It appears as though a critical mass of suspended matter must drop out of surface waters before light penetration is sufficient to support phytoplankton uptake; and in addition mixing must be slow relative to biological uptake. Our observations are certainly reasonable within the context of the known dynamics of the Columbia River region, as the time scale of mixing is likely to be slower here than the rate of removal in continental shelf waters.

If my theory of very slow, limited removal of silicic acid at salinities less than 24 is correct then extrapolation of data back to zero salinity should yield accurate results for silicic acid river values. Original and effective river concentrations for silicic acid were  $114 \pm 4 \mu\text{M}$  and  $30 \pm 10 \mu\text{M}$  respectively (errors represent the 95% confidence interval calculated from the standard deviation of the intercept). Comparing the effective river concentration with the original shows that ~26% of the silicic acid from the original plume core at WCSST09 remains in the mixed waters. These results agree well with previous work. A river discharge for the time period of June-July 1997 of  $5990 \text{ m}^3/\text{s}$  obtained from United States Geological Survey Data and my extrapolated silicic acid values yield an estimate of  $0.18-0.20 \times 10^{10} \text{ mol/month}$  silicic acid. If the annual river discharge of  $8020 \text{ m}^3/\text{s}$  for 1997 obtained again from the United States Geological Survey is used in conjunction with my extrapolated silicic acid values, an estimate of  $2.8-3.1 \times 10^{10} \text{ mol/yr}$  is obtained. This is in reasonable agreement with Columbia River silicic acid fluxes for five different time periods between 1966 and 1981 which ranged from  $\sim 2.7-4.2 \times 10^{10} \text{ mol/yr}$  (Carpenter, 1987).

#### 4.5.4 Gallium (figures 4.5.2.3 and 4.5.2.4)

Dissolved Ga data shown in figures Figure 4.5.2.3 and 4.5.2.4 shows removal, although to a lesser extent than silicic acid. There are insufficient data points in the river end member to determine if removal occurs throughout the entire salinity range studied or simply above 24, as observed for silicic acid. At salinities 24-32 removal of Ga exhibits a very smooth relationship with salinity suggestive of constant river input. The major exception to this pattern is data for the secondary plume where signals are higher than those observed for the primary plume. As the secondary plume is older than the primary, this difference in signal indicates that the Ga concentration in the river was variable at that point. Original and effective river concentrations for Ga are 150pmol/kg and 100pmol/kg respectively. This suggests that ~70% Ga from the original plume core at WCSST09 remains in the mixed waters (Lanthier, 1999). The Ga value of 150pmol/kg, is similar to Ga values (68-250pM) from five eastern American rivers reported by Shiller (1988).

#### 4.5.5 Manganese (figures 4.5.2.5 and 4.5.2.6)

The initial picture emerging from the Mn data indicates significant and rapid removal of Mn at low salinities ( $s=24-25$ ) then very slight removal at salinities above 25. Unlike Ga, values for the secondary plume are lower than those for the primary. Despite on-going removal, Mn values are still elevated above background at WCSST07. If we extrapolate the Mn data back to zero salinity in a manner analogous to Ga and silicic acid however, we see that our initial impression may be somewhat simplistic. Extrapolation gives original and effective river concentrations for Mn of 335nmol/kg and 95nmol/kg respectively. With respect to prior work in this region (Jones and Murray, 1985; Klinkhammer *et al*, 1997) the value of 335nmol/kg appears to be anomalously high. I believe that this indicates entrainment of Mn from the continental shelf; as the river loading of Mn is extensive it is likely that significant quantities of Mn are available to undergo diagenic remobilization and thus be injected into to overlying waters and contribute to this unusually high signal. If this is correct then neither the original or effective values are realistic estimates of Mn in the river. Rather, the effective value must be seen as a combination of both river load and shelf entrained Mn.

Interestingly, a similar situation was observed by van Geen and Luoma (1993) in the San Francisco Bay. These authors extrapolated salinity concentration data from the northern part of the Bay to obtain effective nutrient and trace metal fluxes. Their values were significantly higher than the actual river concentrations and they attributed this to substantial nutrient and trace element fluxes from central and southern San Francisco Bay.

#### 4.5.6 Aluminium (figures 4.5.2.7 and 4.5.2.8)

Al data suggests very rapid removal between  $s=24-25$  then conservative or very slight removal at  $s>25$ . Unlike Mn, there is no significant difference between values for WCSST07 and WCSST08. Original and effective river concentrations for Al were 2nmol/kg and 0.75nmol/kg, respectively, and indicate that ~37% Al from the river at WCSST09 remains in the mixed waters. Interpretation of this data requires acknowledgment of several potential complications. First, it is plausible that Al, like Mn, is influenced by entrainment from shelf sediments. Whilst Al does not undergo redox chemistry, many authors (Measures *et al*, 1984, 1986; Hydes, 1979) have reported elevated Al signals in bottom waters and attributed them to resuspended sediments, thus the values we are seeing are possibly not solely representing river input but also input from sediments. Secondly, the removal of Al may have occurred at salinities lower than those at which we sampled; if this were the case, our estimates of original and effective river concentrations may well be underestimates. The reported average dissolved Al concentration for world rivers is  $1.85 \times 10^3$  nmol/l (Martin and Whitfield, 1983); however removal in estuaries and coastal waters is so dramatic, particularly in highly productive coastal regions, that the importance of fluvial input as a source of dissolved Al the open ocean is extremely variable. Authors such as Hydes and Liss (1977) and Sholkovitz (1976) suggest that ~10-70% of dissolved Al supplied by rivers is lost, making our estimate certainly plausible.

#### 4.5.7 Cadmium

The Cd data, unlike that for Mn, Al and Ga, do not show any significant trends and is thus more difficult to interpret. At first glance the data suggests that the Columbia is not a source of Cd to surface waters of the California Current. There is no significant

signal elevation in the primary or secondary cores, though for all transects there does appear to be a general trend of decreasing concentration with increasing distance from shore. The metal-salinity plot shows a very slight negative curvature which could be interpreted as removal of Cd; however as no significant elevation above background is observed in the lowest salinity waters sampled this is more likely to be due to removal of background Cd by the same on-going processes observed in the upwelling transects which also exhibited a similar decrease in concentration in the offshore direction. It is tempting to attribute the lack of signal to rapid removal of Cd supplied by the river in a manner akin, though more extreme, to that observed for Al. However, when I compare the behavior of Al to Cd in the upwelling regimes, it is clear that Al is removed more rapidly than Cd. One other explanation for the low signal is that riverine concentrations reported by other authors are relatively low and are certainly not significantly greater - and in many cases are less - than California Current background concentrations; it is therefore possible that the Columbia is providing very small quantities of Cd comparable to those observed by other authors (see for example Edmond *et al* (1995), Shiller (1991)), but in this area the input is masked by relatively higher background signals. Finally, it should be acknowledged that the dissolved maximum typically shown by Cd (see for example Duinker *et al*, 1982; Salomons and Kerdiijk, 1986) at low salinities ( $s < 15$ ) was not seen here. Presumably, this reflects the limited range of salinities that we sampled, and must be taken into account for any regression analysis.

Regression of the conservative mixing line back to zero salinity suggests an original river concentration of approximately 0.4nmol/kg. This is at the high end of the range of Cd concentrations reported by authors for other rivers, and it would be interesting to see whether an investigation involving a wider range of salinities would result in a significantly different value to the reported one.

#### 4.5.8 Removal Times

This data indicate the rate of removal for Mn and Ga to be considerably slower than that observed for Al. Several sources of evidence suggest that dissolved Ga is less reactive in seawater than dissolved Al. Orians and Bruland (1988) and Shiller (1988) determined that the seawater molar ratio of Al to Ga is 1-2 orders of magnitude lower than in the average crust; the deep water scavenging residence time based on a simple



vertical advection/diffusion model by Craig (1974) is nearly an order of magnitude shorter for dissolved Al than dissolved Ga; and the inter-ocean fractionation exhibited by dissolved Al is an order of magnitude higher than that of Ga. As a complement to this data, Orians and Bruland (1988) suggested a surface water residence time (central Pacific) for Ga on the order of decades and a surface water residence time (central North Pacific) for Al on the order of 1-4 years. Landing and Bruland (1987) proposed residence times for the scavenging of dissolved Mn in the upper 30m of the North Pacific ranging from 138 days (10km offshore) to 20 years in the central gyre. Whilst this data does not allow a direct comparison of residence times for Ga, Mn and Al in coastal waters to be made, the data does indicate that residence times for the central Pacific for Ga and Mn are comparable whereas the residence time for Al is significantly shorter.

#### **4.6 Summary**

Dissolved Mn, Al and Ga are supplied to North East Pacific coastal surface waters by the Columbia River. Elevated levels of Mn (117nmol/kg), Al (1.1 nmol/kg) and Ga (72 pmol/kg) were observed coincident with the lowest salinity waters (21) sampled. Mn and Ga signals decreased as salinity increased but remained elevated above background up to 200 miles far south of the head of the river. Information obtained from constituent/salinity diagrams allowed the estuarine behavior of these metals to be investigate in more detail. However, a number of complications arose for these diagrams, as the 2 end-member, 1-dimension and consistent temporal conditions they require are potentially violated in the region studied. These types of complications have been observed by other authors, but the plots continue to be used and do give important information that simply needs to be viewed with care. Information obtained from my trace metal/salinity diagrams suggested significant and rapid removal of Mn at low salinities ( $s=21-25$ ) then very slight removal at salinities above 25; data for Ga was unfortunately more limited and thus it was difficult to determine if removal occurred throughout the entire salinity range studied or simply above 24. In contrast, Al was removed significantly faster than either Mn or Ga and did not remain elevated beyond WCSST09; trace metal/salinity diagrams suggested very rapid removal of Al between  $s=24-25$  then conservative or very slight removal at  $s>25$ . It is possible that Mn and Al data may have been influenced by entrainment of trace metals from the sediments and the

observed values were thus not solely representative of riverine input. In addition, the removal of Al may well have been so rapid that estimates of original and effective Al concentrations could be underestimates.

In contrast to Mn, Al and Ga, the Columbia River does not appear to be a significant source of Cd to California Current surface waters; the elevation coincident with low salinity waters that is observed for the other metals is not seen for Cd. However, it is likely that significant quantities of Cd desorbed from the particulate phase at salinities lower than we sampled, thus producing a maximum that I missed.

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## Chapter 5: Conclusions

### 5.1 Summary of the Research

This thesis details the modification of an existing method for the determination of Mn, Al, Cd and Cu in seawater. The method involves pre-concentration on a chelex resin followed by GFAAS determination. The accuracy of the method was determined by analyzing Mn, Cd and Cu in a NASS-3 seawater standard. The results obtained with this method agreed with the certified values. The accuracy of the method for Al could not be determined since there are no seawater standards for this element. The precision of the method was evaluated by examining the RSD's for 10 replicate analyses on the NASS-4 standard. The RSD's for all elements were between 5 and 15%.

This method was used to determine 10 horizontal surface transects for coastal waters off the Californian, Oregon and Washington coasts during June/July 1997. The main purpose of the study was to examine and evaluate sources of trace metals to coastal waters; and I was particularly interested in the impact of fluvial and sediment sources on trace metal distributions. The Pacific Northwest coastline provided an ideal laboratory in which to study these factors. The Columbia River, discharging in to the Pacific at ~42°N, is the second largest river in North America in terms of length and volume and supplies 60% (winter) to 90% (summer) of the freshwater discharged into the Pacific Ocean between San Francisco Bay and the Strait of Juan de Fuca (Simenstad *et al*, 1984, 1991; Huyer, 1974, 1977). I was anticipating seeing a significant response by the metals to the river discharge and I was interested in evaluating both the magnitude and extent of that response. The continental shelf varies greatly in width along the Pacific Northwest coastline, from the Big Sur area where it is extremely narrow to Pt. Arena and Cape Mendocina, California, where it widens significantly. I was interested in examining the impact of benthic sources and the degree to which they correlated with shelf width. Finally, these coastal waters experienced significant upwelling during the study timeframe and I was looking to examine the impact of this upwelling on metal profiles.

Background California Current surface water values were determined for Mn (3-5nmol/kg), Al (0.38-0.65nmol/kg), Cd (0.08-0.30nmol/kg) and Cu (0.79-1.51nmol/kg). These values reflect water that is not impacted by upwelling or riverine processes; and



these data agree well with previous work.

According to this study, the Columbia River is an important source of Mn and Al to California Current surface waters (see tables 5.1-5.4). The highest levels for all transects for Mn and Al were observed coincident with the lowest salinity waters sampled during the study (Mn up to 117nmol/kg; Al up to 1.1nmol/kg), and elevated Mn signals were still observable as far south as Coos Bay, Oregon – almost 300km from the river head. This was similar to the behavior of Ga (data supplied by Lanthier, 1999), with this metal showing a similar high elevation (~49pmol/kg compared with a background signal of ~5-8pmol/kg) coincident with the low salinity waters of WCSST09 and an observable elevation at Coos Bay. In contrast to both Mn and Ga, Al did not show elevation beyond WCSST09. The behavior of these metals in the river plume as it moved south and mixed with surrounding California Current surface waters was studied using metal/salinity plots. Information obtained from these diagrams must be treated with care as a number of complications arose regarding the model that the plots are based upon; and it is likely that the two end-member, one-dimension and consistent temporal model was violated in the study region. The plots suggested significant and rapid removal of Mn at low salinities ( $s=21-25$ ) then very slight removal at salinities above 25; Ga data were somewhat limited and it was thus difficult to determine if removal occurred throughout the entire salinity range studied or simply above 24. Al was removed significantly faster than either Mn or Ga with trace metal/salinity diagrams suggesting extremely rapid removal between  $s=24-25$  then conservative or very slight removal at  $s>25$ . The faster removal of Al relative to that Mn and Ga makes sense in the context of metal residence times; with Orians and Bruland (1988) and Shiller (1988) suggesting that Al has a shorter residence time than Ga, and Landing and Bruland (1987) proposing that Al has a shorter residence time than Mn. A river concentration estimate for Mn (335nmol/kg) was higher than prior work in the region and I believe this reflects entrainment of Mn from the continental shelf - as the river loading of particulate Mn is extensive it is likely that significant quantities of Mn are available to undergo diagenic remobilization and thus be injected into to overlying waters and contribute to this high signal. The river concentration estimate for Al (2nmol/kg), I believe, may be an underestimate as removal of Al is so rapid in this region, and probably occurred at lower salinities than we sampled. In contrast to Mn, Ga

**Table 5.1      Summary of Mn data for WCSST01-WCSST10**

| <b>Transect</b> | <b>Highest upwelling<br/>signal<br/>(nmol/kg)</b> | <b>Fluvial signal<br/>(nmol/kg)</b> | <b>Relative enrichment above<br/>background<br/>(signal/ average background)</b> |
|-----------------|---|-------------------------------------|--|
| WCSST01         | 17.6  | -                                   | 4.4  |
| WCSST02         | 6.2   | -                                   | 1.6  |
| WCSST03         | 39  | -                                   | 9.7  |
| WCSST04         | 13  | -                                   | 3.2  |
| WCSST05         | 25.2  | -                                   | 6.3  |
| WCSST06         | 7.9   | -                                   | 2.0  |
| WCSST07         | -   | 21.8                                | 5.4  |
| WCSST08         | 14.1  | 36.6                                | 9.1  |
| WCSST09         | -   | 115.3                               | 28.8   |
| WCSST10         | 7.2   | -                                   | 1.8  |

- indicates no signal

Background Mn signal = 3-5nmol/kg.

The upwelling data was taken from the regime that showed highest elevation at the transect of interest.

The fluvial data was taken from the lowest salinity waters sampled at the transect of interest.

The relative enrichment gives an indication of the magnitude of signal elevation above the average background signal. No value is given for those signals that are within the background range.

**Table 5.2 Summary of Cd data for WCSST01-WCSST10**

| <b>Transect</b> | <b>Highest upwelling<br/>signal<br/>(nmol/kg)</b> | <b>Fluvial signal<br/>(nmol/kg)</b> | <b>Relative enrichment above<br/>background<br/>(signal/ average background)</b> |
|-----------------|---|-------------------------------------|--|
| WCSST01         | .74   | -                                   | 4.1  |
| WCSST02         | .49   | -                                   | 2.7  |
| WCSST03         | .92   | -                                   | 5.3  |
| WCSST04         | .92   | -                                   | 5.3  |
| WCSST05         | .9  | -                                   | 5  |
| WCSST06         | .47   | -                                   | 2.6  |
| WCSST07         | -   | .13                                 | -  |
| WCSST08         | .48   | .16                                 | -  |
| WCSST09         | -   | .22                                 | -  |
| WCSST10         | .39   | -                                   | 2.2  |

- indicates no signal

Background Cd signal = 0.08-0.30nmol/kg.

The upwelling data was taken from the regime that showed highest elevation at the transect of interest.

The fluvial data was taken from the lowest salinity waters sampled at the transect of interest.

The relative enrichment gives an indication of the magnitude of signal elevation above the average background signal. No value is given for those signals that are within the background range.

**Table 5.3      Summary of Al data for WCSST01-WCSST10**

| <b>Transect</b> | <b>Highest upwelling<br/>signal<br/>(nmol/kg)</b> | <b>Fluvial signal<br/>(nmol/kg)</b> | <b>Relative enrichment above<br/>background<br/>(signal/ average background)</b> |
|-----------------|---|-------------------------------------|--|
| WCSST01         | .55   | -                                   | -  |
| WCSST02         | .54   | -                                   | -  |
| WCSST03         | .74   | -                                   | 1.5  |
| WCSST04         | .70   | -                                   | 1.4  |
| WCSST05         | .66   | -                                   | 1.3  |
| WCSST06         | .55   | -                                   | -  |
| WCSST07         | -   | .52                                 | -  |
| WCSST08         | .63   | .53                                 | -  |
| WCSST09         | -   | 1.01                                | 2.02   |
| WCSST10         | .54   | -                                   | -  |

- indicates no signal

Background Al signal = 0.38-0.65nmol/kg.

The upwelling data was taken from the regime that showed highest elevation at the transect of interest.

The fluvial data was taken from the lowest salinity waters sampled at the transect of interest.

The relative enrichment gives an indication of the magnitude of signal elevation above the average background signal. No value is given for those signals that are within the background range.

**Table 5.4 Summary of Cu data for WCSST01-WCSST10**

| <b>Transect</b> | <b>Highest upwelling<br/>signal<br/>(nmol/kg)</b> | <b>Fluvial signal<br/>(nmol/kg)</b> | <b>Relative enrichment above<br/>background<br/>(signal/ average background)</b> |
|-----------------|---|-------------------------------------|--|
| WCSST01         | 2.67  | -                                   | 2.3  |
| WCSST02         | 2.31  | -                                   | 2.0  |
| WCSST03         | 4.52  | -                                   | 3.9  |
| WCSST04         | 3.79  | -                                   | 3.3  |
| WCSST05         | 4.33  | -                                   | 3.7  |
| WCSST06         | 2.79  | -                                   |  |
| WCSST07         | n/a   | n/a                                 |  |
| WCSST08         | n/a   | n/a                                 |  |
| WCSST09         | n/a   | n/a                                 |  |
| WCSST10         | 3.76  | -                                   |  |

- indicates no signal  
n/a indicates no data available

Background Cu signal = 0.79-2.20nmol/kg.

The upwelling data was taken from the regime that showed highest elevation at the transect of interest.

The relative enrichment gives an indication of the magnitude of signal elevation above the average background signal.

and Al, Cd does not show enrichment in low salinity waters, indeed Cd signals are at background across all transects impacted by the Columbia River. The characteristic Cd maximum observed at low salinities (Edmond *et al*, 1985; Boyle *et al*, 1982; Duinker *et al*, 1982; Salomons and Kerdijk, 1986) was not seen here; this presumably reflects the fact that sampling began at salinities higher than this. Finally, since other authors have reported relatively low riverine concentrations for Cd (Edmond *et al*, 1985; Shiller and Boyle, 1991; Boyle, 1982) it is possible that the Columbia may well be providing small quantities of Cd to California Current waters, but in this area the input is masked by relatively higher background signals.

The Pacific Northwest coastline is also characterized by upwelling (see for example Hickey, 1979; Huyer, 1983; Huyer and Kosro, 1987; Rosenfeld *et al*, 1994), with upwelled water clearly identified by low temperature, high salinity and high nutrient signals. This upwelling supplied significant quantities of Mn (4.6-39.5nmol/kg), Cd (0.32-0.92nmol/kg) and Cu (1.66-4.52nmol/kg) to California Current surface waters; and upwelling signals agreed well with work by authors from this, and other, upwelling regions (see for example Sanudo-Wilhelmy and Flegal, 1991; van Geen and Husby, 1996; Flegal *et al*, 1991). These data agree with my predictions regarding the response of these metals to upwelling. For Mn and Cu, diagenic remobilization and/or sediment resuspension coupled with upwelling explains the elevated signals for these metals. For Cd, the elevation is attributable to transport of enriched bottom water to the surface by upwelling. The Al results were somewhat unexpected in that they showed only slight elevation, and only at two out of the total of twelve upwelling regimes sampled during the study. This suggests either that sediments in this region do not act as a significant source of Al, or that Al is indeed supplied by sediments but is then stripped out of the water at a dramatic rate – faster than that seen for Mn, Cd, Cu, Ga or Fe. Mn and Cu (as well as Cd and Al to a lesser extent) showed a very tight correlation with shelf width with highest signals observed where the shelf was widest and lowest where the shelf was narrow (see Chapter 3, table 3.6.3.1.). This agreed well with Ga data (supplied by Lanthier, 1999) and Fe data (supplied by Bruland, personal communication), which also suggest a correlation between shelf width and signal magnitude. It is interesting to note that Cd signal and magnitude was not as dependent on shelf width; presumably this

reflects the fact that Cd elevation is attributable only to upwelling of Cd-enriched bottom water and is not dependant on benthic sources.

In conclusion, this study provides an in-depth examination and discussion of coastal sources of trace metals to California Current surface waters; and adds well to the growing body of recent work relating to coastal source of trace metals (see for example Cotte-Krief *et al*, 2000). This study indicates that California Current waters receive fluvial input from the Columbia River and this acts as a significant source of Mn and Al. The river may also provide Cd, but fluvial signals are potentially masked by background signals in this area. Fluvial signals elevate Mn up to 28.8 times above background and Al up to 2.02 times above background. A large part of the Pacific Northwest coast is characterized by seasonal upwelling, and this introduces significant quantities of Mn, Cd and Cu to surface waters. Mn is elevated up to 9.7 times above background, Cd up to 5.3 times above background and Cu up to 3.9 times above background. Al, in contrast, does not show significant elevation coincident with upwelling regimes.

Several areas of this work could be extended further. Cross-shelf water column profiles and pore-water analysis would be useful to explore; in particular, this would help answer the question as to whether Al is supplied by upwelling but is then removed so rapidly that we did not see significant elevation, or whether Al does not actually have an important benthic source in this region. It would be useful to extend the area sampled in this study to lower salinity regions within the Columbia River estuary as this would provide a true river end member. Finally, it would interesting to expand the suite of metals investigated.

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# Appendix 1: raw data

## WCSST01

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |      |          |      |      |          |      |          |      |          |      |      |
|-------------------|------------------|----------|---------------|-------------------------|------|----------|------|------|----------|------|----------|------|----------|------|------|
|                   |                  |          |               | Mn                      | Mn   | Mn range | Al   | Al   | Al range | Cd   | Cd range | Cu   | Cu range |      |      |
| 122.319           | 37.061           | 10.832   | 33.34         | 17.6                    | 16.9 | 0.7      | 0.49 | 0.51 | 0.02     | 0.57 | 0.62     | 0.05 | 2.67     | 2.61 | 0.06 |
| 122.277           | 37.036           | 10.986   | 33.35         | 12                      | 12.3 | 0.3      | 0.5  | 0.53 | 0.03     | 0.69 | 0.74     | 0.05 | 2.54     | 2.39 | 0.15 |
| 122.24            | 37.012           | 12.104   | 33.34         | 15.9                    | 15.5 | 0.4      | 0.51 | 0.47 | 0.04     | 0.61 | 0.63     | 0.02 | 1.39     | 1.54 | 0.15 |
| 122.205           | 36.987           | 12.973   | 33.33         | 8.9                     | 8.6  | 0.3      | 0.53 | 0.49 | 0.04     | 0.34 | 0.36     | 0.02 | 1.43     | 1.38 | 0.05 |
| 122.167           | 36.962           | 14.693   | 33.32         | 7                       | 6.8  | 0.2      | 0.53 | 0.5  | 0.03     | 0.28 | 0.26     | 0.02 | 0.97     | 0.8  | 0.17 |
| 122.125           | 36.943           | 13.88    | 33.31         | 6.9                     | 7.2  | 0.3      | 0.52 | 0.53 | 0.01     | 0.26 | 0.28     | 0.02 | 1.07     | 1.2  | 0.13 |
| 122.081           | 36.932           | 13.744   | 33.32         | 6.8                     | 7    | 0.2      | 0.55 | 0.52 | 0.03     | 0.21 | 0.23     | 0.02 | 0.87     | 0.92 | 0.05 |
| 122.021           | 36.916           | 14.168   | 33.31         | 6.2                     | 6.4  | 0.2      | 0.48 | 0.5  | 0.02     | 0.15 | 0.14     | 0.01 | 0.71     | 0.7  | 0.01 |
| 122.016           | 36.858           | 13.559   | 33.31         | 5.8                     | 5.9  | 0.1      | 0.46 | 0.48 | 0.02     | 0.17 | 0.2      | 0.03 | 0.88     | 0.91 | 0.03 |
| 122.018           | 36.815           | 12.698   | 33.31         | 5                       | 4.7  | 0.3      | 0.47 | 0.49 | 0.02     | 0.13 | 0.15     | 0.02 | 0.94     | 0.95 | 0.01 |
| 122.016           | 36.751           | 12.77    | 33.3          | 5.1                     | 4.8  | 0.3      | 0.51 | 0.5  | 0.01     | 0.19 | 0.17     | 0.02 | 0.83     | 0.9  | 0.07 |
| 122.032           | 36.726           | 12.849   | 33.3          | 4                       | 4.4  | 0.4      | 0.48 | 0.49 | 0.01     | 0.15 | 0.13     | 0.02 | 0.87     | 0.84 | 0.03 |
| 122.116           | 36.712           | 13.164   | 33.12         | 4.3                     | 3.9  | 0.4      | 0.48 | 0.46 | 0.02     | 0.16 | 0.18     | 0.02 | 0.88     | 0.92 | 0.04 |

## WCSST02

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |     |          |      |      |          |      |          |      |          |      |
|-------------------|------------------|----------|---------------|-------------------------|-----|----------|------|------|----------|------|----------|------|----------|------|
|                   |                  |          |               | Mn                      | Mn  | Mn range | Al   | Al   | Al range | Cd   | Cd range | Cu   | Cu range |      |
| 121.601           | 36.016           | 33.322   | 11.75         | 2.7                     | 2.9 | 0.2      | 0.48 | 0.5  | 0.02     | 0.48 | 0.45     | 1.7  | 1.73     | 0.03 |
| 121.57            | 36.011           | 33.332   | 11.72         | 4.5                     | 4.6 | 0.1      | 0.49 | 0.5  | 0.01     | 0.4  | 0.42     | 1.72 | 1.81     | 0.09 |
| 121.54            | 36.003           | 33.278   | 11.89         | 4.7                     | 4.3 | 0.4      | 0.49 | 0.5  | 0.01     | 0.43 | 0.46     | 1.8  | 1.92     | 0.12 |
| 121.524           | 35.999           | 33.328   | 11.83         | 5.5                     | 5.4 | 0.1      | 0.5  | 0.52 | 0.02     | 0.45 | 0.43     | 2.29 | 2.31     | 0.02 |
| 121.529           | 35.998           | 33.32787 | 11.8065       | 5.9                     | 6.2 | 0.3      | 0.52 | 0.49 | 0.03     | 0.48 | 0.46     | 2.2  | 2.09     | 0.11 |
| 121.543           | 35.996           | 33.321   | 11.81         | 5.5                     | 5.7 | 0.2      | 0.49 | 0.49 | 0        | 0.44 | 0.45     | 2.21 | 2.27     | 0.06 |
| 121.568           | 35.992           | 33.311   | 11.76         | 5                       | 4.8 | 0.2      | 0.54 | 0.49 | 0.05     | 0.45 | 0.47     | 1.68 | 1.66     | 0.02 |

**WCSST02 cont.**

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Mn  | Mn  | Mn range | Al   | Al   | Al range | Cd   | Cd range | Cu   | Cu range |
|-------------------|------------------|----------|---------------|-----|-----|----------|------|------|----------|------|----------|------|----------|
| 121.644           | 35.972           | 33.259   | 12.38         | 4.6 | 4.8 | 0.2      | 0.49 | 0.51 | 0.02     | 0.45 | 0.03     | 2.17 | 2.06     |
| 121.676           | 35.691           | 33.238   | 12.42         | 4.3 | 4.5 | 0.2      | 0.42 | 0.46 | 0.04     | 0.22 | 0.05     | 2.01 | 1.8      |
| 121.689           | 35.69            | 33.212   | 13            | 4.2 | 4.4 | 0.2      | 0.49 | 0.51 | 0.02     | 0.19 | 0.01     | 2.11 | 1.9      |
| 121.683           | 35.961           | 33.204   | 13.03         | 4.4 | 4.3 | 0.1      | 0.49 | 0.5  | 0.01     | 0.18 | 0.01     | 2.13 | 2        |
| 121.721           | 35.954           | 33.203   | 13.28         | 4.6 | 5   | 0.4      | 0.5  | 0.51 | 0.01     | 0.15 | 0.01     | 1.41 | 1.45     |
| 121.767           | 35.947           | 33.219   | 13.72         | 4.1 | 4.2 | 0.1      | 0.49 | 0.52 | 0.03     | 0.17 | 0.01     | 1.39 | 1.26     |
| 121.855           | 35.949           | 33.222   | 13.85         | 3.7 | 3.8 | 0.1      | 0.5  | 0.53 | 0.03     | 0.17 | 0        | 1.17 | 1.14     |
| 121.943           | 35.947           | 33.258   | 12.59         | 3.4 | 3.4 | 0        | 0.5  | 0.52 | 0.02     | 0.47 | 0.01     | 1.25 | 1.17     |
| 122.029           | 35.946           | 33.249   | 12.56         | 3   | 3.2 | 0.2      | 0.53 | 0.51 | 0.02     | 0.44 | 0.01     | 1.45 | 1.36     |
| 122.119           | 35.942           | 33.299   | 12.01         | 2.9 | 2.6 | 0.3      | 0.49 | 0.52 | 0.03     | 0.43 | 0.01     | 0.96 | 0.94     |
| 122.315           | 35.942           | 33.236   | 14.09         | 2.7 | 3.4 | 0.7      | 0.5  | 0.54 | 0.04     | 0.2  | 0.02     | 1.73 | 1.81     |
| 122.447           | 35.946           | 33.146   | 14.03         | 2.8 | 2.7 | 0.1      | 0.54 | 0.52 | 0.02     | 0.13 | 0.02     | 0.95 | 0.99     |
| 122.554           | 35.966           | 33.117   | 14.5          | 3.2 | 3   | 0.2      | 0.49 | 0.53 | 0.04     | 0.15 | 0.04     | 1.32 | 1.46     |
| 122.559           | 35.969           | 33.117   | 14.39         | 5.5 | 5.2 | 0.3      | 0.49 | 0.52 | 0.03     | 0.11 | 0.01     | 1.02 | 0.94     |
| 122.601           | 36.016           | 33.322   | 11.75         | 5.3 | 5.4 | 0.1      | 0.5  | 0.52 | 0.02     | 0.22 | 0.07     | 2.22 | 2.1      |
| 122.57            | 36.011           | 33.332   | 11.72         | 5   | 5.2 | 0.2      | 0.5  | 0.51 | 0.01     | 0.4  | 0.02     | 2.23 | 2.34     |

**WCSST03**

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Mn   | Mn   | Mn range | Al   | Al   | Al range | Cd   | Cd range | Cu   | Cu range |
|-------------------|------------------|----------|---------------|------|------|----------|------|------|----------|------|----------|------|----------|
| 122.572           | 37.551           | 32.629   | 12.9          | 34.2 | 35.1 | 0.9      | 0.71 | 0.72 | 0.01     | 0.87 | 0.09     | 4.2  | 4        |
| 122.565           | 37.542           | 32.638   | 12.96         | 33.2 | 34.9 | 1.7      | 0.68 | 0.66 | 0.02     | 0.85 | 0        | 3.99 | 4.12     |
| 122.542           | 37.523           | 33.199   | 11.12         | 34   | 33.3 | 0.7      | 0.69 | 0.72 | 0.03     | 0.89 | 0.01     | 4.02 | 3.89     |
| 122.54            | 37.522           | 33.222   | 11.02         | 28.1 | 26.6 | 1.5      | 0.69 | 0.71 | 0.02     | 0.86 | 0.01     | 4.02 | 3.89     |
| 122.521           | 37.502           | 33.341   | 10.83         | 33   | 34   | 1        | 0.69 | 0.71 | 0.02     | 0.86 | 0.01     | 3.98 | 3.89     |
| 122.522           | 37.501           | 33.341   | 10.71         | 33.4 | 34   | 0.6      | 0.71 | 0.74 | 0.03     | 0.89 | 0.05     | 4.2  | 3.99     |

**WCSST03 cont.**

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Mn   | Mn   | Mn range | Al   | Al   | Al range | Cd   | Cd range | Cu   | Cu range |
|-------------------|------------------|----------|---------------|------|------|----------|------|------|----------|------|----------|------|----------|
| 122.539           | 37.503           | 33.291   | 10.74         | 36.7 | 34.4 | 2.3      | 0.71 | 0.73 | 0.02     | 0.92 | 0.82     | 4.31 | 4.52     |
| 122.561           | 37.504           | 33.059   | 11.72         | 33.2 | 34.2 | 1        | 0.7  | 0.73 | 0.03     | 0.86 | 0.83     | 4.21 | 3.99     |
| 122.658           | 37.501           | 32.91    | 12.91         | 37   | 39.5 | 2.5      | 0.74 | 0.72 | 0.02     | 0.85 | 0.89     | 4.44 | 4.21     |
| 122.707           | 37.501           | 33.015   | 12.95         | 37   | 36.2 | 0.8      | 0.74 | 0.73 | 0.01     | 0.65 | 0.67     | 4.37 | 4.23     |
| 122.744           | 37.503           | 33.071   | 12.28         | 17.1 | 16.2 | 0.9      | 0.71 | 0.72 | 0.01     | 0.54 | 0.56     | 3.03 | 2.93     |
| 122.789           | 37.502           | 33.173   | 12.01         | 16.2 | 16.7 | 0.5      | 0.69 | 0.65 | 0.04     | 0.61 | 0.58     | 2.97 | 2.84     |
| 122.822           | 37.503           | 33.313   | 11.42         | 14.7 | 14.2 | 0.5      | 0.68 | 0.66 | 0.02     | 0.64 | 0.66     | 3.2  | 3.33     |
| 122.864           | 37.501           | 33.217   | 11.45         | 10.2 | 10.8 | 0.6      | 0.67 | 0.65 | 0.02     | 0.69 | 0.66     | 2.57 | 2.71     |
| 122.895           | 37.497           | 33.1     | 11.66         | 24.7 | 25.1 | 0.4      | 0.67 | 0.67 | 0        | 0.74 | 0.76     | 3.45 | 3.54     |
| 122.926           | 37.5             | 32.989   | 11.72         | 23.9 | 24.7 | 0.8      | 0.65 | 0.67 | 0.02     | 0.71 | 0.74     | 3.16 | 3.09     |
| 122.981           | 37.505           | 32.84    | 12.65         | 24.6 | 23.8 | 0.8      | 0.65 | 0.67 | 0.02     | 0.69 | 0.64     | 3.02 | 3.12     |
| 123.015           | 37.505           | 32.826   | 13.66         | 24.3 | 24   | 0.3      | 0.66 | 0.67 | 0.01     | 0.51 | 0.48     | 3.48 | 3.38     |
| 123.075           | 37.52            | 32.813   | 13.55         | 4.4  | 4.5  | 0.1      | 0.66 | 0.63 | 0.03     | 0.33 | 0.37     | 2    | 2.06     |
| 123.111           | 37.537           | 32.891   | 13.13         | 4.4  | 4    | 0.4      | 0.58 | 0.6  | 0.02     | 0.28 | 0.3      | 1.89 | 1.94     |
| 123.153           | 37.564           | 33.11    | 11.02         | 4.2  | 4    | 0.2      | 0.55 | 0.58 | 0.03     | 0.25 | 0.24     | 2.04 | 2.01     |
| 123.178           | 37.596           | 32.998   | 11.01         | 4.2  | 4.5  | 0.3      | 0.57 | 0.56 | 0.01     | 0.27 | 0.25     | 2.41 | 2.32     |
| 123.198           | 37.602           | 33.12    | 11            | 4.1  | 4.3  | 0.2      | 0.56 | 0.54 | 0.02     | 0.18 | 0.16     | 1.99 | 1.8      |
| 123.201           | 37.657           | 33.152   | 11.02         | 3.8  | 4    | 0.2      | 0.57 | 0.54 | 0.03     | 0.14 | 0.15     | 1.95 | 2.01     |
| 123.212           | 37.724           | 33.198   | 11.03         | 4.2  | 4.1  | 0.1      | 0.51 | 0.53 | 0.02     | 0.1  | 0.12     | 2.1  | 1.99     |
| 123.314           | 37.799           | 33.202   | 12.03         | 4    | 3.8  | 0.2      | 0.51 | 0.5  | 0.01     | 0.29 | 0.34     | 2.89 | 2.83     |

**WCSST04**

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |      |          |      |      |          |      |      |          |      | Cu<br>range |          |
|-------------------|------------------|----------|---------------|-------------------------|------|----------|------|------|----------|------|------|----------|------|-------------|----------|
|                   |                  |          |               | Mn                      | Mn   | Mn range | Al   | Al   | Al range | Cd   | Cd   | Cd range | Cu   | Cu          | Cu range |
| 123.52            | 38.717           | 33.59    | 8.55          | 9.9                     | 9.7  | 0.2      | 0.63 | 0.67 | 0.02     | 0.69 | 0.71 | 0.02     | 2.48 | 2.53        | 0.05     |
| 123.478           | 38.705           | 33.599   | 8.55          | 9.8                     | 9.7  | 0.1      | 0.64 | 0.66 | 0.05     | 0.61 | 0.67 | 0.06     | 2.44 | 2.5         | 0.06     |
| 123.46            | 38.701           | 33.595   | 8.72          | 11.2                    | 11.6 | 0.4      | 0.65 | 0.67 | 0.16     | 0.83 | 0.81 | 0.02     | 3.77 | 3.61        | 0.16     |
| 123.478           | 38.7             | 33.597   | 8.55          | 12                      | 12.6 | 0.6      | 0.61 | 0.63 | 0.25     | 0.88 | 0.89 | 0.01     | 3.51 | 3.79        | 0.28     |
| 123.497           | 38.7             | 33.599   | 8.51          | 11.1                    | 11.3 | 0.2      | 0.62 | 0.56 | 0.29     | 0.85 | 0.89 | 0.04     | 3.37 | 3.26        | 0.11     |
| 123.51            | 38.7             | 33.59    | 8.49          | 10.1                    | 9.8  | 0.3      | 0.64 | 0.62 | 0.26     | 0.88 | 0.86 | 0.02     | 2.93 | 2.84        | 0.09     |
| 123.525           | 38.701           | 33.589   | 8.46          | 10.1                    | 10.6 | 0.5      | 0.64 | 0.65 | 0.21     | 0.86 | 0.87 | 0.01     | 2.71 | 2.54        | 0.17     |
| 123.551           | 38.703           | 33.57    | 8.62          | 10.6                    | 10.4 | 0.2      | 0.65 | 0.67 | 0.22     | 0.89 | 0.86 | 0.03     | 2.99 | 3.13        | 0.14     |
| 123.568           | 38.704           | 33.54    | 8.73          | 10.2                    | 9.6  | 0.6      | 0.61 | 0.66 | 0.24     | 0.9  | 0.93 | 0.03     | 2.83 | 2.7         | 0.13     |
| 123.583           | 38.705           | 33.53    | 8.78          | 10                      | 10.4 | 0.4      | 0.65 | 0.67 | 0.22     | 0.89 | 0.88 | 0.01     | 2.79 | 2.98        | 0.19     |
| 123.633           | 38.707           | 33.521   | 8.99          | 12.5                    | 13   | 0.5      | 0.66 | 0.7  | 0.22     | 0.92 | 0.86 | 0.06     | 3.56 | 3.34        | 0.22     |
| 123.67            | 38.708           | 33.498   | 9.16          | 10.1                    | 9.9  | 0.2      | 0.65 | 0.67 | 0.21     | 0.88 | 0.82 | 0.06     | 2.66 | 2.58        | 0.08     |
| 123.685           | 38.708           | 33.494   | 9.27          | 8                       | 8.1  | 0.1      | 0.65 | 0.64 | 0.23     | 0.87 | 0.84 | 0.03     | 2.53 | 2.45        | 0.08     |
| 123.698           | 38.709           | 33.501   | 9.24          | 7.7                     | 7.7  | 0        | 0.65 | 0.66 | 0.1      | 0.76 | 0.77 | 0.01     | 2.97 | 3.25        | 0.28     |
| 123.733           | 38.71            | 33.482   | 9.51          | 8                       | 8.3  | 0.3      | 0.62 | 0.64 | 0.01     | 0.63 | 0.6  | 0.03     | 2.31 | 2.17        | 0.14     |
| 123.784           | 38.71            | 33.447   | 9.59          | 6.9                     | 7.1  | 0.2      | 0.6  | 0.57 | 0.05     | 0.62 | 0.59 | 0.03     | 2.06 | 1.99        | 0.07     |
| 123.79            | 38.712           | 33.408   | 9.57          | 5.4                     | 7.6  | 2.2      | 0.62 | 0.59 | 0.02     | 0.57 | 0.55 | 0.02     | 1.91 | 2.1         | 0.19     |
| 123.914           | 38.71            | 33.083   | 11.06         | 3.3                     | 3.2  | 0.1      | 0.63 | 0.65 | 0.07     | 0.58 | 0.67 | 0.09     | 0.96 | 0.94        | 0.02     |
| 123               | 38.722           | 33.018   | 11.55         | 3.1                     | 3    | 0.1      | 0.6  | 0.63 | 0.24     | 0.39 | 0.48 | 0.09     | 1.7  | 1.82        | 0.12     |
| 123.993           | 38.719           | 32.874   | 11.72         | 2.6                     | 2.7  | 0.1      | 0.6  | 0.58 | 0.28     | 0.3  | 0.4  | 0.1      | 2    | 2.1         | 0.1      |
| 124.149           | 38.774           | 32.758   | 13.01         | 4.6                     | 5    | 0.4      | 0.56 | 0.55 | 0.36     | 0.19 | 0.25 | 0.06     | 1.97 | 1.91        | 0.06     |
| 124.197           | 38.798           | 32.781   | 12.9          | 4.8                     | 4.8  | 0        | 0.57 | 0.54 | 0.34     | 0.2  | 0.22 | 0.02     | 2.1  | 2.23        | 0.13     |
| 124.255           | 38.837           | 32.846   | 12.74         | 2.5                     | 2.6  | 0.1      | 0.53 | 0.55 | 0.34     | 0.21 | 0.24 | 0.03     | 2.03 | 1.97        | 0.06     |
| 124.324           | 38.878           | 32.891   | 12.54         | 6.3                     | 2.8  | 3.5      | 0.55 | 0.53 | 0.34     | 0.19 | 0.2  | 0.01     | 1.82 | 1.79        | 0.03     |
| 124.386           | 38.917           | 32.797   | 12.91         | 4.7                     | 4.4  | 0.3      | 0.51 | 0.52 | 0.38     | 0.14 | 0.18 | 0.04     | 1.79 | 1.7         | 0.09     |
| 124.411           | 38.937           | 32.784   | 12.91         | 4.9                     | 5    | 0.1      | 0.51 | 0.53 | 0.41     | 0.12 | 0.16 | 0.04     | 1.98 | 2.04        | 0.06     |

**WCSST05**

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Mn    | Mn   | Mn range | Al   | Al   | Al range | Cd   | Cd   | Cd range | Cu   | Cu   | Cu range |
|-------------------|------------------|----------|---------------|-------|------|----------|------|------|----------|------|------|----------|------|------|----------|
| 124.139           | 40.051           | 33.518   | 9.29          | 24    | 22   | 2        | 0.58 | 0.55 | 0.03     | 0.76 | 0.78 | 0.02     | 3.9  | 4.01 | 0.11     |
| 124.071           | 40.015           | 33.535   | 8.92          | 25.45 | 28   | 2.55     | 0.62 | 0.64 | 0.02     | 0.88 | 0.83 | 0.05     | 3.5  | 3.34 | 0.16     |
| 124.074           | 40.006           | 33.536   | 9.16          | 23.2  | 25.2 | 2        | 0.6  | 0.63 | 0.03     | 0.79 | 0.8  | 0.01     | 3.22 | 3.1  | 0.12     |
| 124.111           | 40.007           | 33.417   | 9.35          | 8.7   | 9.1  | 0.4      | 0.61 | 0.59 | 0.02     | 0.72 | 0.69 | 0.03     | 3.89 | 3.64 | 0.25     |
| 124.129           | 40.007           | 33.426   | 9.3           | 7     | 6.8  | 0.2      | 0.63 | 0.65 | 0.02     | 0.72 | 0.69 | 0.03     | 2.84 | 2.73 | 0.11     |
| 124.137           | 40.007           | 33.458   | 9.13          | 6.7   | 6.8  | 0.1      | 0.64 | 0.66 | 0.02     | 0.73 | 0.7  | 0.03     | 2.78 | 2.64 | 0.14     |
| 124.144           | 40.006           | 33.42    | 9.27          | 7     | 6.5  | 0.5      | 0.6  | 0.58 | 0.02     | 0.72 | 0.7  | 0.02     | 2.63 | 2.78 | 0.15     |
| 124.204           | 40.006           | 33.366   | 9.74          | 7.5   | 7.9  | 0.4      | 0.59 | 0.56 | 0.03     | 0.7  | 0.69 | 0.01     | 4.01 | 4.33 | 0.32     |
| 124.252           | 40.006           | 33.373   | 9.71          | 8.6   | 8.9  | 0.3      | 0.6  | 0.58 | 0.02     | 0.75 | 0.73 | 0.02     | 2.01 | 2.11 | 0.1      |
| 124.299           | 40.006           | 33.418   | 9.67          | 9.9   | 9.6  | 0.3      | 0.58 | 0.6  | 0.02     | 0.72 | 0.75 | 0.03     | 2.25 | 2.31 | 0.06     |
| 124.306           | 40.007           | 33.465   | 9.18          | 10.2  | 9.1  | 1.1      | 0.59 | 0.58 | 0.01     | 0.75 | 0.78 | 0.03     | 2.31 | 2.12 | 0.19     |
| 124.406           | 40.006           | 33.463   | 8.89          | 10.9  | 10.2 | 0.7      | 0.57 | 0.55 | 0.02     | 0.77 | 0.74 | 0.03     | 2.06 | 1.93 | 0.13     |
| 124.458           | 40.005           | 33.148   | 9.94          | 7.9   | 7.6  | 0.3      | 0.56 | 0.58 | 0.02     | 0.67 | 0.7  | 0.03     | 1.45 | 1.4  | 0.05     |
| 124.495           | 40.001           | 33.087   | 10.52         | 6.5   | 6.9  | 0.4      | 0.55 | 0.54 | 0.01     | 0.5  | 0.55 | 0.05     | 1.18 | 1.1  | 0.08     |
| 124.504           | 39.997           | 33.067   | 10.78         | 4.6   | 4.9  | 0.3      | 0.54 | 0.56 | 0.02     | 0.51 | 0.44 | 0.07     | 1.72 | 1.61 | 0.11     |
| 124.508           | 39.997           | 33.06    | 10.81         | 2.9   | 3.2  | 0.3      | 0.59 | 0.56 | 0.03     | 0.56 | 0.39 | 0.17     | 1.51 | 1.44 | 0.07     |
| 124.553           | 39.998           | 32.915   | 11.22         | 2     | 2.1  | 0.1      | 0.57 | 0.6  | 0.03     | 0.55 | 0.58 | 0.03     | 1.65 | 1.6  | 0.05     |
| 124.559           | 39.999           | 32.925   | 11.35         | 1.8   | 2.2  | 0.4      | 0.58 | 0.56 | 0.02     | 0.56 | 0.45 | 0.11     | 1.93 | 1.81 | 0.12     |
| 124.674           | 40.005           | 32.76    | 13.04         | 2.6   | 2.3  | 0.3      | 0.54 | 0.55 | 0.01     | 0.13 | 0.1  | 0.03     | 2.01 | 1.94 | 0.07     |
| 124.786           | 40.01            | 32.709   | 13.1          | 2.4   | 2.7  | 0.3      | 0.6  | 0.57 | 0.03     | 0.16 | 0.19 | 0.03     | 1.87 | 1.89 | 0.02     |
| 124.896           | 40.012           | 32.528   | 12.58         | 2     | 2.3  | 0.3      | 0.54 | 0.52 | 0.02     | 0.09 | 0.11 | 0.02     | 1.23 | 1.15 | 0.08     |
| 124.992           | 40.004           | 32.404   | 13.2          | 1.9   | 2.2  | 0.3      | 0.54 | 0.53 | 0.01     | 0.1  | 0.14 | 0.04     | 2.25 | 2.09 | 0.16     |
| 125.121           | 39.994           | 32.157   | 15.62         | 3.5   | 3.4  | 0.1      | 0.53 | 0.51 | 0.02     | 0.08 | 0.09 | 0.01     | 1.58 | 1.47 | 0.11     |
| 125.127           | 39.993           | 32.156   | 15.62         | 3.4   | 3.7  | 0.3      | 0.53 | 0.54 | 0.01     | 0.09 | 0.09 | 0        | 1.96 | 2    | 0.04     |
| 125.136           | 39.992           | 32.16    | 15.65         | 2.8   | 3.2  | 0.4      | 0.53 | 0.54 | 0.01     | 0.09 | 0.12 | 0.03     | 1.79 | 1.87 | 0.08     |
| 125.162           | 39.993           | 32.173   | 15.8          | 3.15  | 3.4  | 0.25     | 0.55 | 0.49 | 0.06     | 0.08 | 0.12 | 0.04     | 1.28 | 1.3  | 0.02     |

# WCSST06

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |     |          |      |      |          |      |          |      |          |
|-------------------|------------------|----------|---------------|-------------------------|-----|----------|------|------|----------|------|----------|------|----------|
|                   |                  |          |               | Mn                      | Mn  | Mn range | Al   | Al   | Al range | Cd   | Cd range | Cu   | Cu range |
| 124.233           | 41.256           | 33.03    | 12.23         | 9.6                     | 9.4 | 0.2      | 0.6  | 0.63 | 0.03     | 0.5  | 0.51     | 2.02 | 2.12     |
| 124.203           | 41.233           | 32.705   | 13.1          | 6.7                     | 6.5 | 0.2      | 0.59 | 0.57 | 0.02     | 0.37 | 0.39     | 2.3  | 2.44     |
| 124.169           | 41.203           | 32.798   | 13.68         | 7.2                     | 7.5 | 0.3      | 0.55 | 0.53 | 0.02     | 0.32 | 0.37     | 2.95 | 2.77     |
| 124.193           | 41.201           | 32.758   | 13.28         | 6.4                     | 6.2 | 0.2      | -    | -    | -        | 0.33 | 0.35     | 2.67 | 2.79     |
| 124.225           | 41.2             | 32.877   | 12.98         | 7.9                     | 7.7 | 0.2      | 0.54 | 0.51 | 0.03     | 0.4  | 0.36     | 2.54 | 2.61     |
| 124.248           | 41.199           | 32.915   | 12.2          | 7.5                     | 7.2 | 0.3      | 0.51 | 0.5  | 0.01     | 0.38 | 0.4      | 2.26 | 2.21     |
| 124.347           | 41.203           | 32.755   | 13.34         | 6.5                     | 6.7 | 0.2      | 0.54 | 0.52 | 0.02     | 0.36 | 0.36     | 2.14 | 2.03     |
| 124.404           | 41.203           | 32.581   | 11.73         | 6.8                     | 6.9 | 0.1      | 0.54 | 0.56 | 0.02     | 0.35 | 0.32     | 2.2  | 2.01     |
| 124.445           | 41.201           | 32.205   | 11.95         | 6.9                     | 6.4 | 0.5      | 0.52 | 0.55 | 0.03     | 0.3  | 0.33     | 1.99 | 2.12     |
| 124.526           | 41.197           | 31.847   | 12.38         | 6.8                     | 6.7 | 0.1      | 0.5  | 0.48 | 0.02     | 0.27 | 0.26     | 2.25 | 2.12     |
| 124.618           | 41.2             | 31.977   | 12.55         | 6                       | 6.3 | 0.3      | 0.51 | 0.48 | 0.03     | 0.2  | 0.22     | 0.86 | 0.73     |
| 124.675           | 41.195           | 31.905   | 12.69         | 5.8                     | 5.5 | 0.3      | 0.5  | 0.49 | 0.01     | 0.25 | 0.26     | 1.88 | 1.7      |
| 124.775           | 41.198           | 32.064   | 13.61         | 3.6                     | 4   | 0.4      | 0.53 | 0.52 | 0.01     | 0.17 | 0.15     | 1.59 | 1.68     |
| 124.892           | 41.202           | 32.068   | 13.83         | 4.3                     | 4.4 | 0.1      | 0.53 | 0.55 | 0.02     | 0.14 | 0.16     | 0.98 | 1        |
| 125.046           | 41.203           | 32.192   | 13.68         | 4.5                     | 4.7 | 0.2      | 0.53 | 0.55 | 0.02     | 0.13 | 0.15     | 2.05 | 2        |
| 125.197           | 41.203           | 32.288   | 14.31         | 5.1                     | 4.9 | 0.2      | 0.52 | 0.55 | 0.03     | 0.14 | 0.12     | 1.94 | 1.89     |
| 125.33            | 41.201           | 32.124   | 13.24         | 3.6                     | 3.8 | 0.2      | 0.52 | 0.56 | 0.04     | 0.12 | 0.15     | 2.1  | 2.28     |

**WCSST07**

| Longitude<br>(°W) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |             |      |             |      |             | Cd<br>range |
|-------------------|------------------|----------|---------------|-------------------------|-------------|------|-------------|------|-------------|-------------|
|                   |                  |          |               | Mn                      | Mn<br>range | Al   | Al<br>range | Cd   | Cd<br>range |             |
| 124.536           | 42.558           | 27.513   | 16.96         | 10                      | 10.3        | 0.49 | 0.47        | 0.22 | 0.29        | 0.07        |
| 124.498           | 42.522           | 27.943   | 16.53         | 21.15                   | 22          | 0.48 | 0.48        | 0    | 0.24        | 0.04        |
| 124.486           | 42.499           | 28.52    | 16.18         | 23.5                    | 24.6        | 0.47 | 0.48        | 0.01 | 0.19        | 0.04        |
| 124.499           | 42.498           | 27.88    | 16.68         | 23.8                    | 24.7        | 0.5  | 0.53        | 0.03 | 0.17        | 0.02        |
| 124.544           | 42.497           | 27.306   | 17.29         | 23.95                   | 23.2        | 0.51 | 0.54        | 0.03 | 0.18        | 0.01        |
| 124.589           | 42.499           | 26.995   | 17.49         | 26                      | 24.7        | 0.52 | 0.49        | 0.03 | 0.17        | 0.02        |
| 124.609           | 42.499           | 26.953   | 17.66         | 25.9                    | 25.4        | 0.49 | 0.51        | 0.02 | 0.13        | 0.05        |
| 124.66            | 42.5             | 26.668   | 17.82         | 27.1                    | 23.7        | 0.48 | 0.47        | 0.01 | 0.19        | 0.04        |
| 124.664           | 42.501           | 26.585   | 17.86         | 27.95                   | 29          | 0.49 | 0.53        | 0.04 | 0.17        | 0.01        |
| 124.754           | 42.502           | 25.922   | 18.05         | 28.55                   | 24          | 0.53 | 0.55        | 0.02 | 0.19        | 0.03        |
| 124.857           | 42.503           | 25.714   | 18.13         | 17.85                   | 18.2        | 0.52 | 0.55        | 0.03 | 0.17        | 0           |
| 124.991           | 42.506           | 25.923   | 18.31         | 31.9                    | 33          | 0.5  | 0.49        | 0.01 | 0.14        | 0.04        |
| 125.127           | 42.501           | 26.482   | 18.1          | 21.95                   | 21.5        | 0.54 | 0.5         | 0.04 | 0.13        | 0           |
| 125.297           | 42.499           | 25.561   | 18.3          | 21.55                   | 22.1        | 0.55 | 0.52        | 0.03 | 0.11        | 0.02        |
| 125.513           | 42.506           | 25.864   | 18.26         | 21.2                    | 20.2        | 0.53 | 0.54        | 0.01 | 0.11        | 0.01        |
| 125.647           | 42.505           | 26.254   | 18.3          | 22.15                   | 21.9        | 0.52 | 0.5         | 0.02 | 0.13        | 0.03        |
| 125.777           | 42.503           | 26.786   | 18.16         | 17.45                   | 17.1        | -    | -           | -    | 0.14        | 0.01        |



**WCST08**

| Longitude | Latitude | Salinity | Temp. | Concentration (nmol/kg) |      |          |      |      |          |      |          |      |
|-----------|----------|----------|-------|-------------------------|------|----------|------|------|----------|------|----------|------|
|           |          |          |       | Mn                      | Mn   | Mn range | Al   | Al   | Al range | Cd   | Cd range |      |
| 124.178   | 44.238   | 31.959   | 12.49 | 18.1                    | 18.8 | 0.7      | 0.55 | 0.56 | 0.01     | 0.18 | 0.16     | 0.02 |
| 124.146   | 44.201   | 32.554   | 10.25 | 14.4                    | 14.1 | 0.3      | 0.61 | 0.63 | 0.02     | 0.45 | 0.48     | 0.03 |
| 124.217   | 44.201   | 31.684   | 13.52 | 16.4                    | 16.8 | 0.4      | 0.58 | 0.56 | 0.02     | 0.25 | 0.24     | 0.01 |
| 124.321   | 44.203   | 31.564   | 14.61 | 17.6                    | 17.9 | 0.3      | 0.46 | 0.5  | 0.04     | 0.27 | 0.26     | 0.01 |
| 124.455   | 44.203   | 30.225   | 15.61 | 23.4                    | 23.8 | 0.4      | 0.47 | 0.49 | 0.02     | 0.29 | 0.26     | 0.03 |
| 124.622   | 44.196   | 30       | 15.97 | 23.6                    | 22.4 | 1.2      | 0.45 | 0.49 | 0.04     | 0.29 | 0.27     | 0.02 |
| 124.744   | 44.202   | 29.988   | 16.66 | 27.5                    | 26.4 | 1.1      | 0.46 | 0.52 | 0.06     | 0.23 | 0.25     | 0.02 |
| 124.951   | 44.203   | 28.394   | 18.19 | 33.2                    | 34.3 | 1.1      | 0.5  | 0.49 | 0.01     | 0.18 | 0.2      | 0.02 |
| 125.048   | 44.202   | 27.541   | 18.69 | 35.9                    | 37.3 | 1.4      | 0.51 | 0.54 | 0.03     | 0.15 | 0.17     | 0.02 |
| 125.183   | 44.206   | 28.808   | 18.69 | 28.1                    | 29.2 | 1.1      | 0.5  | 0.53 | 0.03     | 0.16 | 0.14     | 0.02 |
| 125.267   | 44.212   | 31.637   | 17.92 | 5.3                     | 5    | 0.3      | 0.48 | 0.53 | 0.05     | 0.13 | 0.1      | 0.03 |

**WCST09**

| (°W)    | (°W)   | (°C)  | Mn    | Mn range | Al   | Al range | Cd   | Cd range |
|---------|--------|-------|-------|----------|------|----------|------|----------|
| 124.032 | 46.048 | 16    | 46.5  | 48.2     | 0.52 | 0.53     | 0.24 | 0.25     |
| 124.018 | 46.027 | 16.49 | 55.3  | 54.1     | 0.63 | 0.66     | 0.22 | 0.24     |
| 123.999 | 46     | 16.76 | 55.5  | 56       | 0.62 | 0.64     | 0.19 | 0.2      |
| 124.067 | 46     | 16.59 | 63.6  | 66.1     | 0.89 | 0.95     | 0.22 | 0.27     |
| 124.186 | 46.001 | 16.36 | 93.7  | 97.8     | 1    | 1.05     | 0.24 | 0.25     |
| 124.262 | 46.001 | 16.3  | 115.6 | 113.2    | 1.15 | 1.04     | 0.22 | 0.21     |

| Longitude | Latitude | Salinity | Temp. | Concentration (nmol/kg) |       |      |      |          |      | Cd range |          |      |
|-----------|----------|----------|-------|-------------------------|-------|------|------|----------|------|----------|----------|------|
|           |          |          |       | (°W)                    | (°W)  | (°C) | Mn   | Mn range | Al   |          | Al range | Cd   |
| 124.347   | 45.994   | 21.182   | 16.22 | 113.4                   | 117.2 | 3.8  | 0.99 | 1.03     | 0.04 | 0.21     | 0.22     | 0.01 |
| 124.428   | 45.999   | 24.005   | 16.66 | 109.5                   | 106.2 | 3.3  | 0.97 | 1.04     | 0.07 | 0.27     | 0.25     | 0.02 |
| 124.577   | 46.001   | 28.338   | 17.85 | 41                      | 38    | 3    | 0.83 | 0.81     | 0.02 | 0.2      | 0.17     | 0.03 |
| 124.685   | 45.999   | 29.872   | 18.63 | 44.9                    | 42.8  | 2.1  | 0.65 | 0.68     | 0.03 | 0.2      | 0.22     | 0.02 |
| 124.806   | 45.999   | 28.32    | 19.31 | 68.8                    | 72.2  | 3.4  | 0.59 | 0.57     | 0.02 | 0.19     | 0.23     | 0.04 |
| 125.039   | 46.006   | 30.117   | 18.86 | 72.3                    | 75.6  | 3.3  | 0.58 | 0.59     | 0.01 | 0.15     | 0.11     | 0.04 |
| 125.161   | 45.999   | 30.946   | 18.83 | 13.5                    | 13.9  | 0.4  | 0.51 | 0.47     | 0.04 | 0.1      | 0.15     | 0.05 |

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |     |          |      |      |          |      |      |          |      |      |          |
|-------------------|------------------|----------|---------------|-------------------------|-----|----------|------|------|----------|------|------|----------|------|------|----------|
|                   |                  |          |               | Mn                      | Mn  | Mn range | Al   | Al   | Al range | Cd   | Cd   | Cd range | Cu   | Cu   | Cu range |
| 124.523           | 47.51            | 15.818   | 30.54         | 6.6                     | 6.4 | 0.2      | 0.56 | 0.53 | 0.03     | 0.22 | 0.24 | 0.02     | 0.98 | 0.91 | 0.07     |
| 124.556           | 47.58            | 16.093   | 30.77         | 6.6                     | 6.3 | 0.3      | 0.52 | 0.54 | 0.02     | 0.25 | 0.26 | 0.01     | 0.91 | 0.95 | 0.04     |
| 124.579           | 47.519           | 14.538   | 30.06         | 6.5                     | 6.3 | 0.2      | 0.55 | 0.59 | 0.04     | 0.28 | 0.25 | 0.03     | 1.2  | 1.27 | 0.07     |
| 124.602           | 47.637           | 14.673   | 30.1          | 6.4                     | 6.2 | 0.2      | 0.59 | 0.56 | 0.03     | 0.35 | 0.39 | 0.04     | 1.52 | 1.63 | 0.11     |
| 124.61            | 47.662           | 15.676   | 21.14         | 6                       | 5.8 | 0.2      | 0.53 | 0.55 | 0.02     | 0.39 | 0.37 | 0.02     | 1.61 | 1.5  | 0.11     |
| 124.637           | 47.708           | 16.957   | 27.31         | 6.1                     | 5.9 | 0.2      | 0.49 | 0.53 | 0.04     | 0.4  | 0.42 | 0.02     | 1.57 | 1.47 | 0.1      |
| 124.658           | 47.758           | 16.304   | 28.37         | 5.5                     | 5.6 | 0.1      | 0.52 | 0.54 | 0.02     | 0.33 | 0.31 | 0.02     | 2.22 | 2.15 | 0.07     |
| 124.678           | 47.801           | 14.695   | 29.8          | 5.6                     | 5.7 | 0.1      | 0.5  | 0.51 | 0.01     | 0.27 | 0.29 | 0.02     | 2.58 | 2.67 | 0.09     |
| 124.775           | 47.89            | 15.991   | 21.92         | 6                       | 6.2 | 0.2      | 0.54 | 0.51 | 0.03     | 0.36 | 0.38 | 0.02     | 1.6  | 1.62 | 0.02     |
| 124.785           | 47.935           | 15.874   | 26.62         | 5.9                     | 6   | 0.1      | 0.53 | 0.52 | 0.01     | 0.31 | 0.33 | 0.02     | 1.68 | 1.82 | 0.14     |
| 124.798           | 48.013           | 16.06    | 29.98         | 5.8                     | 5.7 | 0.1      | 0.5  | 0.51 | 0.01     | 0.29 | 0.27 | 0.02     | 2.51 | 2.3  | 0.21     |
| 124.818           | 48.085           | 15.108   | 29.48         | 6                       | 5.9 | 0.1      | 0.47 | 0.49 | 0.02     | 0.29 | 0.32 | 0.03     | 2.46 | 2.34 | 0.12     |
| 124.823           | 48.163           | 15.643   | 28.95         | 6.5                     | 6.3 | 0.2      | 0.49 | 0.52 | 0.03     | 0.28 | 0.24 | 0.04     | 2.39 | 2.22 | 0.17     |
| 124.841           | 48.221           | 15.611   | 29.36         | 6.3                     | 6.5 | 0.2      | 0.5  | 0.5  | 0        | 0.3  | 0.33 | 0.03     | 2.39 | 2.48 | 0.09     |

**WCSST10 cont.**

| Longitude<br>(°N) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |     |          |      |          |      |          |          |
|-------------------|------------------|----------|---------------|-------------------------|-----|----------|------|----------|------|----------|----------|
|                   |                  |          |               | Mn                      | Mn  | Mn range | Al   | Al range | Cd   | Cd range | Cu range |
| 124.842           | 48.296           | 15.958   | 29.35         | 6.6                     | 6.3 | 0.3      | 0.48 | 0.45     | 0.03 | 0.38     | 0.11     |
| 124.895           | 48.302           | 16.626   | 29.34         | 7.2                     | 7   | 0.2      | 0.51 | 0.47     | 0.04 | 0.39     | 0.15     |
| 124.89            | 48.347           | 15.656   | 29.31         | 6.9                     | 6.7 | 0.2      | 0.5  | 0.47     | 0.03 | 0.35     | 0.09     |

**WCSST 7b**

| Longitude<br>(°W)       | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Mn   | Mn   | Mn range | Al   | Al range | Cd   | Cd range |
|-------------------------|------------------|----------|---------------|------|------|----------|------|----------|------|----------|
| Concentration (nmol/kg) |                  |          |               |      |      |          |      |          |      |          |
| 124.527                 | 42.563           | 31.77    | 12.76         | 13.7 | 13.2 | 0.5      | 0.49 | 0.53     | 0.23 | 0.26     |
| 124.529                 | 42.579           | 31.704   | 12.66         | 13.6 | 14.1 | 0.5      | 0.47 | 0.48     | 0.22 | 0.24     |
| 124.532                 | 42.614           | 31.676   | 12.53         | 14.5 | 14.9 | 0.4      | 0.52 | 0.52     | 0.24 | 0.22     |
| 124.536                 | 42.619           | 31.685   | 12.52         | 13.5 | 13.2 | 0.3      | 0.51 | 0.53     | 0.19 | 0.2      |
| 124.569                 | 42.694           | 32.135   | 12.44         | 13.4 | 13.7 | 0.3      | 0.49 | 0.51     | 0.24 | 0.21     |
| 124.667                 | 42.753           | 31.347   | 12.95         | 14.6 | 14.1 | 0.5      | 0.48 | 0.45     | 0.22 | 0.24     |
| 124.634                 | 42.857           | 31.047   | 13.55         | 19.6 | 19.2 | 0.4      | 0.4  | 0.45     | 0.21 | 0.22     |
| 124.567                 | 43.05            | 31.915   | 13.01         | 14   | 14.2 | 0.2      | 0.47 | 0.49     | 0.19 | 0.22     |
| 124.544                 | 43.154           | 30.217   | 14.89         | 14.9 | 14.5 | 0.4      | 0.49 | 0.51     | 0.15 | 0.17     |
| 124.498                 | 43.248           | 29.601   | 15.94         | 15.9 | 15.5 | 0.4      | 0.45 | 0.46     | 0.16 | 0.19     |
| 124.467                 | 43.326           | 28.461   | 16.82         | 16.8 | 16.7 | 0.1      | 0.52 | 0.49     | 0.15 | 0.13     |

**WCSST8b**

| Longitude<br>(°W) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |      |          |      |          |      |      | Cd<br>range |      |
|-------------------|------------------|----------|---------------|-------------------------|------|----------|------|----------|------|------|-------------|------|
|                   |                  |          |               | Mn                      | Mn   | Mn range | Al   | Al range | Cd   |      |             |      |
| 124.119           | 44.854           | 30.773   | 13.62         | 18.7                    | 19   | 0.3      | 0.47 | 0.49     | 0.02 | 0.24 | 0.22        | 0.02 |
| 124.082           | 44.96            | 29.609   | 15.43         | 13.9                    | 14.3 | 0.4      | 0.54 | 0.52     | 0.02 | 0.22 | 0.19        | 0.03 |
| 124.051           | 45.106           | 30.007   | 14.41         | 14.3                    | 13.9 | 0.4      | 0.51 | 0.54     | 0.03 | 0.21 | 0.22        | 0.01 |
| 124.037           | 45.207           | 27.804   | 16.93         | 15.4                    | 15.2 | 0.2      | 0.51 | 0.55     | 0.04 | 0.23 | 0.26        | 0.03 |
| 124.04            | 45.216           | 28.373   | 16.44         | 15                      | 15.1 | 0.1      | 0.53 | 0.51     | 0.02 | 0.27 | 0.24        | 0.03 |

**WCSST09b**

| Longitude<br>(°W) | Latitude<br>(°W) | Salinity | Temp.<br>(°C) | Concentration (nmol/kg) |      |          |      |      |          |      | Cd<br>range |      |
|-------------------|------------------|----------|---------------|-------------------------|------|----------|------|------|----------|------|-------------|------|
|                   |                  |          |               | Mn                      | Mn   | Mn range | Al   | Al   | Al range | Cd   |             |      |
| 124.119           | 44.854           | 30.773   | 13.62         | 15.4                    | 15.5 | 0.1      | 0.53 | 0.5  | 0.03     | 0.21 | 0.23        | 0.02 |
| 124.082           | 44.96            | 29.609   | 15.43         | 13.5                    | 13.3 | 0.2      | 0.5  | 0.52 | 0.02     | 0.19 | 0.15        | 0.04 |
| 124.051           | 45.106           | 30.007   | 14.41         | 8.2                     | 8    | 0.2      | 0.62 | 0.59 | 0.03     | 0.16 | 0.19        | 0.03 |
| 124.037           | 45.207           | 27.804   | 16.93         | 11.8                    | 12.1 | 0.3      | 0.48 | 0.5  | 0.02     | 0.25 | 0.22        | 0.03 |
| 124.04            | 45.216           | 28.373   | 16.44         | 8.9                     | 8    | 0.9      | 0.5  | 0.51 | 0.01     | 0.26 | 0.24        | 0.02 |

Note that all salinity and temperature data were supplied by Ken Bruland (University of California at Santa Cruz).

Note that all highlighted data are presented in Table 3.6.3.1.