ALUMINUM AND IRON DISTRIBUTIONS IN THE CENTRAL AND WESTERN NORTH PACIFIC OCEAN: RESULTS FROM THE 2002 INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION CRUISE

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By

Matthew T. Brown

Thesis Committee:

Christopher Measures, Chairperson
Eric H. DeCarlo
Telu Yuan-Hui Li
DEDICATION

I dedicate this thesis to my Mom, Leslie Hawes. Thank you for giving me the gift of life and thank you for believing in me when even I did not. You are eternally my greatest teacher and I will always love you.
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I extend my deepest gratitude to the following people who helped me along the way and made the past three years some of the best of my life.

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ABSTRACT

Specifically, the goal of this thesis research was to examine the effects of Asian dust deposition to the waters of the NW Pacific on both surface and deep-water biogeochemistry, particularly trace metal cycling. The elements of interest to this research were Al, as a tracer of atmospheric dust input to the surface ocean, and Fe, as the flux of this biologically required trace element is largely regulated by transport and deposition of mineral aerosols.

Samples were collected during the Intergovernmental Oceanographic Commission NW Pacific Cruise of May-June 2002. Both continuous surface water sampling while the ship is underway and station vertical profile sampling were performed using trace-metal clean techniques. Both Al and Fe were determined on-board using flow injection analysis utilizing in-line 8-hydroxyquinoline pre-concentration. In addition, ancillary parameters such as nutrients, temperature, and salinity were also measured.

Surface water Al over the cruise track ranged from less than 0.1 nM to greater than 10 nM with maximum values appearing near the Hawaiian Islands. Surface water Fe concentrations ranged from approximately 0.15 nM in waters of the subarctic N. Pacific to values greater than 1.2 nM. Al and Fe vertical profile results showed significant variability among stations with features observed such as a subsurface Al
maximum at select stations and a Fe minimum in the suboxic intermediate waters of the subarctic N. Pacific.

The surface water Al results are used to estimate atmospheric dust fluxes to the waters of the central and western N. Pacific and these fluxes are compared with contemporary dust flux models. In addition, Fe surface and vertical profile data are used to assess biological limitation in the subarctic N. Pacific and explore the relationships between biological limitation and atmospheric dust flux to the surface ocean. Finally, vertical profiles are discussed in terms of geochemical processes and possible signals of atmospheric dust flux in the deep ocean.
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Chapter 1: Introduction

1.1. A Global Picture

It has become increasingly clear that the atmospheric and oceanic geochemical reservoirs are intimately related and that fluxes between these two reservoirs may have a significant impact on global climate as well as species diversity. Thus, it is then crucial that the magnitude and characterization of fluxes between the atmosphere and oceans be well understood in terms of climate-forcing species.

Large-scale cyclic variations in both global climate and glaciation characterize the past one million years of the Earth's climate history, the late Quaternary period, with glacial-interglacial cycles of about 100,000 years (Imbrie, 1992). Vast expanses of ice sheets covered much of North America during cold "ice age" periods as temperatures dropped dramatically. During interglacial periods, Northern Hemisphere glaciation decreased as temperatures warmed.

It is well known that the concentration of atmospheric carbon dioxide (CO₂) has varied with glacial/interglacial cycles (Figure 1.1; Petit et al., 1999). Glacial periods reveal lower concentrations of atmospheric CO₂ while interglacial periods had higher atmospheric CO₂ levels. During glacial periods such as the Last Glacial Maximum (~18,000 yrs. ago) atmospheric CO₂ was roughly 180-200 ppmv while interglacial periods such as the Holocene (~ last 10,000 yrs.) show increased levels near 280 ppmv.
In recent years a putative link between global climate and fluxes of atmospheric dust have been investigated. Research has clearly shown dramatic increases in fluxes of atmospheric dust during glacial maxima recorded in sediments and ice cores (DeAngelis et al., 1987; Kumar et al., 1995). As will be discussed later in more detail, it has been argued that this enhanced flux of atmospheric dust, and, specifically, iron (Fe), to ocean surface waters results in the lower atmospheric carbon dioxide levels seen during glacial maxima (Martin and Fitzwater, 1988).

However, in the years since the Industrial Revolution the combination of fossil-fuel burning and deforestation have severely perturbed the natural cyclicity of atmospheric carbon dioxide. According to the Intergovernmental Panel on Climate Change 2001 Report, atmospheric CO$_2$ has increased more than 30% since pre-Industrial times and has been increasing at an unprecedented rate of 0.4% yr$^{-1}$ since 1998. CO$_2$ is an atmospheric greenhouse gas and plays a central role in regulating global climate. It is then crucial that possible significant effects of increased atmospheric CO$_2$ are understood through climate modeling.

In order to develop accurate and realistic models of future climate change, it is imperative that the possible biogeochemical effects of atmospheric dust deposition, particularly trace species contained therein, to the world’s oceans be investigated and characterized.
1.2. Trace Elements

In recent years it has become clear that trace metals such as Cu, Fe, and Zn play a key role in biological processes, evolution, and possibly climate change. During the evolution of primordial life forms the chemistry and availability of trace metals led to the acquisition of distinct chemical functions for these elements usually dealing with the storage, transport, and transfer of energy through redox reactions. Several trace metal species in the first transition row (e.g. Co, Cu, Fe, Mn) have pairs of oxidation states differing by only one electron and requiring relatively small amounts of free energy to transition between them (Frausto da Silva and Williams, 1994). These oxidation-state pairs are therefore suitable candidates for redox-reaction energy functions (de Baar and La Roche, 2002).

The advent of photosynthesis and the evolution of free oxygen had a notable effect on the abundance of trace metal species by creating an oxidizing atmosphere and ocean. This oxidation process had consequences that are believed to be central to global climate processes, in particular the oxidation of readily soluble Fe (II) to sparingly soluble Fe (III). This oxidation reduced the concentration of available Fe in the world's oceans by orders of magnitude (de Baar and de Jong, 2001).

The biological necessity of some trace metal species is well understood. For example, Fe is crucial in the electron transport of the photosynthetic apparatus and, thus, energy supply to the cell. Moreover, Fe is required in the enzymes nitrate reductase and
nitrite reductase for the utilization of the major nutrient nitrate (Timmermans et al., 1994). Lastly, in order to achieve full utilization of bicarbonate, the major chemical species of CO$_2$ in seawater, Zn is a necessary component of carbonic anhydrase (Morel et al., 1994).

Sources of trace metal species to oceanic waters include both "new" sources from external inputs as well as "regenerated" sources from recycling within the euphotic zone and deep-water regeneration. Wet and dry deposition of aerosols, vertical mixing and upwelling, inputs from rivers, bottom sediments, and hydrothermal vents, and biogenic recycling of cellular material are the major sources of Fe in the world's oceans (Wells et al., 1995). However, in deep oceanic regions far from any landmass, the atmospheric deposition of aerosols is the major source of external iron to the biologically productive surface waters.

The above demonstrate(s) that understanding the magnitude and biogeochemical effects of atmospheric dust fluxes and, hence, trace metal inputs to the world's oceans via eolian dust deposition is important.

1.3. **HNLC Regions and the Iron Hypothesis**

A unique oceanographic feature of the Antarctic Southern Ocean, the subarctic North Pacific, and the equatorial Pacific is an non-utilized reservoir of the major plant nutrients NO$_3^-$, PO$_4^{3-}$, and SiO$_3^{2-}$ during periods when primary productivity would be
expected to remove them. These nutrients are needed by phytoplankton to convert inorganic carbon in the form of aqueous carbon dioxide to organic carbon, an energy source for the oceanic food web. It was found that the amounts of euphotic zone nutrients delivered via upwelling or remineralization in these three regions of the ocean were significantly greater than the amounts of nutrients assimilated and utilized by phytoplankton (Martin et al., 1991). This results in "lower-than-expected chlorophyll" production levels (Martin et al., 1991). The Southern Ocean, subarctic N. Pacific, and the equatorial Pacific were thus coined High-Nutrient, Low-Chlorophyll (HNLC) regions.

The first suggestion that Fe availability might limit primary production was made by Gran in 1931 (de Baar, 1994). However, due to a lack of suitably-sensitive methodologies for iron determinations and a lack of trace-metal clean sampling techniques, little progress was made in furthering these ideas. However, in recent years John Martin's iron hypothesis put forth the argument that in these HNLC regions low levels of Fe appeared to be limiting the ability of photosynthetic organisms to utilize available macronutrients (NO$_3^-$, PO$_4^{3-}$, SiO$_3^{2-}$) (Martin and Fitzwater, 1988).

The iron hypothesis was tested in the subarctic Northeast Pacific (Martin and Fitzwater, 1988). Briefly, unfiltered (including resident-phytoplankton) euphotic zone (20 m) water samples were collected and nmol amounts of dissolved Fe were added. Within one week these Fe additions resulted in four-fold increases in chlorophyll...
concentrations and the nearly complete utilization of available nitrate. Control samples (no Fe added), however, showed only 25% of the available nitrate to be assimilated. The nutrient uptake patterns were similar with respect to PO_4^{3-}.

Similar experiments were performed in the equatorial Pacific and the Ross Sea of the Antarctic Southern Ocean (Martin et al., 1991). Significant increases in phytoplankton growth rates, POC, and nutrient uptake were observed. In addition, observations from the equatorial Pacific bottle enrichment experiments suggested that more C fixation by phytoplankton per unit of major nutrients may occur when Fe is abundant.

The extrapolation of results from shipboard and laboratory experiments to an open-ocean ecosystem, however, was strongly criticized. Thus, in order to represent a true ecosystem-scale response, the first open-ocean Fe fertilization experiments were performed in the equatorial Pacific whereby a patch of ocean was enriched with ~4 nM addition of Fe. This resulted in a doubling of plant biomass, a threefold increase in chlorophyll, and a fourfold increase in plant production inside the enriched patch. (Martin et al., 1994). Similar experiments have since been performed in the Southern Ocean with similar results.

Martin et al. argued that in the HNLC waters of the Southern Ocean, the subarctic N. Pacific, and the equatorial Pacific that the Fe supplies from local sources (upwelling, advection, remineralization) in the surface waters were rapidly used up. In addition, it
was postulated that the atmospheric inputs of Fe to these regions were insufficient to meet the demands of phytoplankton resulting from upwelling of the major plant nutrients such as NO$_3^-$. The role of Fe in plant metabolism for photosynthetic and electron transport, chlorophyll synthesis, detoxification of reactive oxygen species, and, most importantly, nitrate reduction, is well-understood (Sunda and Huntsman, 1995). Therefore, the relationship between low levels of Fe and high standing stocks of NO$_3^-$ is clear.

Furthermore, Martin et al. (1991) also hypothesized a link between the previously-mentioned glacial period increases in atmospheric dust fluxes during glacial periods and lower glacial atmospheric CO$_2$ levels (Figure 1.1). It was postulated that the enhanced dust flux from the atmosphere to the oceans during glacial periods stimulated phytoplankton productivity and photosynthesis, thus causing the drawdown of carbon dioxide from the atmosphere to the oceans. This quite likely led to the decreased atmospheric CO$_2$ levels proxied in the sedimentary and ice core records. Thus, the exact role that atmospheric dust deposition plays in the stimulation and phytoplankton activity and subsequent atmospheric carbon dioxide drawdown needs to be investigated.

It is quite likely that other trace species could contribute to nutrient utilization as well. Both zinc and manganese were shown to limit the reproductive rates of marine phytoplankton (Brand et al., 1983). In addition, zinc was shown to limit the induction of carbonic anhydrase in the marine diatom *Thalassiosira weissflogii*, hence limiting
dissolved inorganic carbon exploitation (Lane and Morel, 2000). Finally, nickel was demonstrated to limit \textit{T. weissflogii} as well, as the Ni-containing enzyme urease is necessary for urea catabolism in this diatom (Price and Morel, 1991). Thus, the apparent relationship between the delivery of reactive trace species to the surface ocean and global climate change needs to be investigated in order to develop a comprehensive understanding of the mechanisms involved.

1.4. \textit{Atmospheric Dust Deposition}

As mentioned previously, the atmospheric input of Fe is generally considered to be the dominant external source of iron to surface waters of the open ocean. In the subarctic N. Pacific, 84-93\% of the external Fe transport is due to atmospheric dust deposition (Martin et al., 1989). In addition, estimates of the Fe input in surface waters near Hawaii showed greater than 90\% of total Fe input being due to atmospheric deposition (Donaghay et al., 1991).

Over the Pacific Ocean the mid- and high latitudes of the N. Pacific generally have the highest atmospheric dust concentrations due to seasonal transport of Asian dust, mainly loess from the Gobhi desert area of China. These concentrations are usually highest in the spring due to very unstable air masses creating strong winds following the passage of intense cold fronts across the Gobhi desert region. The dust concentrations are low in the summer and winter and moderate during the fall. The equatorial region of
the Pacific is generally a low dust area with only the occasional spring pulse of Asian
dust reaching the area (Duce and Tindale, 1991).

The significant relationship between Fe limitation in HNLC waters and the
atmospheric input of iron was detailed in the previous section. However, even with such
a strong impetus to characterize and quantify atmospheric dust fluxes to the world's
oceans, the task is quite difficult. First, the flux of atmospheric dust is quite episodic in
nature with the majority of deposition occurring in a relatively short period of time. At
Midway Island in the central N. Pacific, for example, nearly 50% of the total yearly flux
occurred in two weeks (Prospero et al., 1989). Thus, the short duration of research
cruises makes it doubtful that direct shipboard measurements will ever yield an accurate
measure of atmospheric dust fluxes.

Second, a lack of sampling sites leads to insufficient spatial coverage. Remote
island sampling is effective yet limited. Third, estimates of dust fluxes via sediment traps
are hindered by the unresolved role of advection in under-supplying material to upper
water and over-supplying materials to near-bottom traps. Finally, satellite-based remote
sensing, which does provide global coverage of atmospheric dust events, is not currently
able to distinguish between atmospheric dust and other atmospheric aerosols such as soot
and ash.

Despite these problems and lack of extensive data sets, Duce et al. (1991),
hereafter referred to as the Duce model, calculated global atmospheric mineral dust flux
estimates to surface waters of the world's oceans (Figure 1.2). Their calculations were based on direct eolian dust measurements at a variety of land-based sampling stations and extrapolation of these measurements out into the oceans where measurements were not available. First, the estimates indicate that nearly 90% of the total atmospheric dust flux to the world oceans occurs in the Northern Hemisphere, likely due to the large deserts and dry regions in the Arabian Peninsula, Asia, India, and N. Africa. Secondly, the highest estimated dust fluxes are to the surface waters of the eastern central Atlantic and the far western N. Pacific. These two particular high-dust input regions are due to the Saharan and Gobhi desert dusts, respectively.

1.5. The MADCOW Model

In a somewhat inverse approach the problem of accurately measuring atmospheric dust fluxes to the oceans can perhaps be solved by investigating the dissolved chemical signals that persist in the surface ocean after the dust has been deposited. In this manner the magnitude of the dust deposition may be traced to the magnitude of the chemical signal in the surface water. Four factors control the magnitude of the dissolved chemical signal in ocean surface waters resulting from atmospheric dust deposition: the relative abundance of the chemical element of interest in the dust, its fractional solubility in the surface ocean, the depth of the surface mixed layer into which the dust is deposited, and the element's residence time within the mixed layer (Measures and Vink, 2000).
Measures and Brown (1996) presented a model, the measurement of Al for dust calculation in oceanic waters, herein referred to as MADCOW, whereby surface water aluminum concentrations were used to estimate the flux of atmospheric dust to the surface ocean. Aluminum is an ideal tracer of atmospheric dust flux for several reasons. First, previous work has shown that aluminum has a mixed surface water layer residence time of 3-5 years in the oligotrophic N. Pacific and 6.5 years in the oligotrophic Sargasso Sea (Orians and Bruland, 1986; Jickells et al., 1994). Due to rapid removal via scavenging on the surface of organisms (Moran and Moore, 1992), surface water aluminum concentrations in regions receiving small fluxes of atmospheric dust are on the order of a few nM. These low concentrations provide a suitable low-aluminum background to model atmospheric dust input.

Second, Al is a primary and relatively constant component of continental crust, approximately 8.1% by weight (Taylor, 1964). Due to intense scavenging in coastal regions, riverine Al inputs, although large, are prevented from becoming significant sources of Al to open-ocean waters (Hydes, 1989). Thus, in the open ocean the major source of Al is atmospheric input of continentally-derived dust. Finally, aluminum, unlike Fe or Mn, is biologically inert in the surface waters with the exception of passive scavenging by particles and, in addition, has no redox chemistry or speciation change.

The MADCOW model postulates that the input of dissolved Al is entirely due to the dissolution of atmospheric dust and, further, that the dissolved Al concentration in the
mixed layer is in steady state. Specifically, the input of dissolved Al, entirely through atmospheric dust deposition and dissolution, is balanced by the removal of Al via particle scavenging through particle flux from biological processes. Several assumptions were made in order to calculate atmospheric dust fluxes from surface water Al concentrations.

First, the mixed layer residence time of aluminum was assumed to be 5 years. As mentioned previously, the surface water residence time of Al in the oligotrophic N Pacific and Sargasso Sea has been found to be 3-5 years and 6.5 yrs, respectively. However, in higher productivity regions such as upwelling and coastal zones, the residence time of Al is likely to be somewhat shorter. Thus, in these regions the model will probably underestimate dust input.

Second, the partial solubility of atmospheric dust was assumed to be 1.5-5% from previous laboratory work (Prospero et al., 1987). Further supporting these findings, Sato (2002) found the partial solubility of aluminum in Asian dust around Hawaii to be ~4.5%.

Third, the mixed layer depth was assumed to be 30 m. In areas where the true mixed layer depth is deeper than 30 m the model will underestimate the eolian dust flux. The assumption of a relatively shallow mixed layer is because Al will be removed from surface waters during spring and summer months when increasing insolation and lower wind stress lead to the shallowest surface mixed layers.

Finally, since the model calculates deposition into surface waters, the advection of those surface waters into regions of higher or lower inputs will result in errors when
assessing the geographic deposition pattern. The short residence time of Al will to some degree help mitigate this error but results in highly advective regions will be more problematic.

Thus, using these assumptions one can create an equation in which the atmospheric dust inputs necessary to maintain the existing surface water Al concentrations against removal due to particle scavenging can be calculated:

\[ G = \frac{(A \times 0.2 \times M \times 1000)}{(D \times S)} \]

where \( G \) = dust input (g m\(^{-2}\) yr\(^{-1}\)), \( A \) = Al concentration (mol/L), \( S \) = fractional solubility,

\( D \) = concentration of Al in dust (moles g\(^{-1}\))

\( M \) = mixed layer depth (meters)

\( 0.2 \) = scavenging fraction (yr\(^{-1}\)) based on 5 yr. Al residence time

The model has been calibrated using previously determined surface water Al concentrations in regions close to areas where independent dust depositions have also been measured (Measures and Vink, 2000). Dust deposition model estimates were compared to these independent estimates (Figure 1.3). It should be pointed out that the independent dust estimates are made via direct measurement at atmospheric sampling stations by measuring the flux of lithogenic material in sediment traps or from independent model estimates based on known atmospheric dust loads and precipitation/scavenging estimates. Over a range of three orders of magnitude of dust
deposition the MADCOW model agrees with the independent dust deposition estimates to within a factor of three.

1.6. 2002 IOC Cruise Rationale and MADCOW Application to NW Pacific

The 2002 IOC cruise to the western and central N. Pacific (Figure 1.4) was designed to examine the effects of atmospheric input to a region of the N. Pacific where the Duce model indicates significant fluxes of atmospheric dust, 1-10 g m$^{-2}$ yr$^{-1}$, of dust deposition.

It is well-known, however, that in the far western subarctic Pacific near 50$^\circ$N, 170$^\circ$E is a broad area, the western end of the HNLC subarctic N. Pacific region, where summer surface nitrate levels are in excess of 10 $\mu$M, a relatively large standing-stock of post-bloom nitrate. (Figure 1.5). Spring pre-bloom nitrate levels in the same area are in excess of 20 $\mu$M (Figure 1.6), indicating a roughly 10 $\mu$M nitrate removal.

Duce model dust deposition to the region range from 1-10 g m$^{-2}$ yr$^{-1}$. Assuming an average mineral aerosol Fe content of 1 mmol Fe g$^{-1}$ dust (Wedepohl, 1995), a 5% partial Fe solubility (Zhu et al., 1997), and a 50-m mixed layer, the modeled dust deposition would result in a 1.7-17 nM dissolved Fe flux per year to the surface mixed layer. Utilizing an average C:N ratio of 6.63 and a limiting C:Fe ratio of $10^5$ (Sunda and Huntsman, 1995), this amount of Fe should be sufficient to allow for the drawdown of more than all of the observed ~20 $\mu$M NO$_3^-$ surface water. Consequently, either the Duce
model is over-estimating dust and Fe input to the western subarctic N. Pacific or nutrient utilization in the region is being limited by something other than Fe.

To investigate this region a cruise track was designed to sample across the large atmospheric dust deposition gradients predicted by the Duce model. The cruise was scheduled for the month of May, towards the end of the traditional high-dust season when the maximum annual deposition would be expected to be visible in the surface waters.

Underway surface Al and Fe concentrations were determined continuously along the cruise track. The Al concentrations have been used in the MADCOW model to estimate dust deposition fluxes to the central and western N. Pacific. Comparison has been made with the Duce model estimates of dust flux to the western and central N. Pacific. This underway sampling was combined with selected vertical profile sampling. Nine vertical Al and Fe profiles were obtained at various points along the cruise track (Figure 1.4) to investigate the pathways by which the surface dust deposition signal is incorporated into the deeper waters of the N. Pacific.

Thus, the major objectives of this thesis stemming from the 2002 IOC cruise results were the following:

1. Using surface water Al concentrations, estimate eolian dust flux estimates to the surface waters of the central and western N. Pacific and compare the estimates with established Duce model values.
2. Examine the variability in surface water Fe concentrations along the cruise track in relation to dust deposition estimates and explore, particularly in the HNLC western subarctic N. Pacific, the relationship between dust deposition, Fe, and nitrate.

3. Examine trace metal profiles at deep-water stations for biogeochemical signals of atmospheric dust in the water column and hydrographic changes.
Chapter 2: Methods

2.1. Sample Collection

Sample collection took place during the Intergovernmental Oceanographic Commission central and western N. Pacific cruise aboard the R/V Melville. The ship departed Osaka, Japan on May 1, 2002 and arrived in Honolulu, Hawaii on June 6, 2002. During the cruise nine vertical profile stations of varying depths (shallow, intermediate, and deep) were occupied and continuous underway surface sampling occurred during the transits between the stations (Figure 1.4).

Vertical profile station samples were collected from 30-L Go-Flo bottles attached to Kevlar line. These samples were immediately filtered using 0.4μm acid leached Nucleopore polycarbonate membrane sandwich filters as described elsewhere (Johnson et al., 1997). Aliquots of these Go-Flo samples were collected into 125ml high density polyethylene bottles and stored unacidified in the dark at 4°C until the Al and Fe determinations were made, usually within 12 hours.

The continuous underway surface samples were collected using the towed fish method described by Vink et al. (2000). This method allows for continuous uncontaminated sampling of surface water while the ship is underway at full speed. Briefly, a bathythermograph (BT) was towed from a boom extending about 5 meters from the side of the ship. Teflon-lined polyethylene tubing (Nalgene 489 PE) was clamped
along the side of the BT with the head of the tubing extending approximately 7 cm ahead of the nose of the BT. This polyethylene tubing was run loosely along the towing line up to the deck of the ship where it was connected to C-Flex tubing which runs through a Masterflex Console Drive peristaltic pump. On the other side of the pump was a further length of Teflon-lined polyethylene tubing taking seawater into the lab. The outlet of the tube was passed through the top of a class-100 laminar flow bench positioned over a sink.

The flow of surface seawater into the laminar flow hood above the sink was split into a filtered and an unfiltered line. Water was filtered by passing through an in-line Pall Gelman 0.2μm Suporcap Capsule filter. Prior to the use of these filters, 3M HCl was cycled through the filter for 24 hrs. The filters then were leached with the 3M HCl for 1 week. At the end of this week 18 MΩ-resistivity deionized water was cycled through the filters for 24 hrs. The filters were then stored with the MQ inside until use. The in-line filters were changed every day. A tee from this filtered line delivered surface seawater into the automated flow injection analytical system for Al and Fe determinations. (Vink et al., 2000).

2.2. Trace Metal Determinations

Determinations were made using in-line preconcentration methods with fluorometric detection for Al (Resing and Measures, 1994) and spectrophotometric detection for Fe (Measures et al., 1995), respectively. The Al and Fe FIA system in
conjunction with the surface seawater inlet design is shown in Figure 2.1. All analytical reagents were prepared fresh each day.

2.2.1 Reagents

Acids: ultrapure hydrochloric acid (HCl, 6M) and ultrapure acetic acid (17.4M) were prepared by sub-boiling distillation in a quartz finger distillation apparatus (Kuehner et al., 1972). Reagents were prepared using 18 MΩ-resistivity deionized water (DI) in a class-100 laminar flow bench to minimize contamination.

Ammonia: ultrapure ammonia (NH₄OH, 4-5M) was produced by isopiestic distillation. Two wide-mouth 1-L bottles each containing 800 ml of DI water and an acid clean magnetic stirrer were placed in a 5-L tupperware snap-tight container containing approx. 2 L of 30% NH₄OH. After three days with a daily stirring to each 1-L bottle the DI becomes approx. 4-5 M NH₄OH.

Brij-35: 5% Brij-35 was prepared by diluting approx. 40 ml of 30% Brij-35 (Sigma Diagnostics) with DI to a final volume of 250 ml.

Hydrogen Peroxide: 5% H₂O₂ was prepared by adding diluting approx. 40 ml of 30% H₂O₂ (J.T. Baker, Ultrex Ultrapure) with DI to a final volume of 250 ml.
DPD: 0.046 M N,N-dimethyl-p-phenylenediamine dihydrochloride (DPD) was prepared by dissolving 1 gram of DPD (Aldrich, cat#21,923-1) into 100ml DI water. In addition, 100 µl of 6M HCl was added to the solution to inhibit oxidation of the solution by air as it sits in the bottle.

Buffers: 2M ammonium acetate buffer was prepared by adding approx. 115 ml of ultrapure 6 M Acetic acid (HC₂H₅COO⁻) to 1.76 moles of ultrapure NH₄OH. The mixture was then diluted to 1-L with DI and the pH adjusted using small additions of ammonia or acetic acid to achieve a pH of 6.3±0.1 for the Fe system or 6.0±0.1 for the Al system. The sample buffer used for in-line pH adjustment of the acidified fish sample used the same pH 6.3 2M ammonium acetate buffer. The Fe reaction buffer was prepared by adding 1.26 ml of a 55 mM triethylenetetramine solution (Fluka Chemika, cat# 90460) and 2.4 mL of the 5% Brij-35 solution to 1 L of the pH 6.3 ammonium acetate buffer.

Lumogallion /buffer reagent: lumogallion stock solution was prepared by adding 50 mg of lumogallion (Pfaltz & Bauer) into 30 ml of DI. Lumogallion/buffer reagent was prepared by adding 5 ml of lumogallion stock solution to 500 ml of pH 6.0 ammonium acetate buffer.
Column-cleaned seawater: low Fe and Al seawater was prepared by passing 0.2μm-filtered seawater buffered to pH 5.2 (by the addition of 400 μl 6M HCl and 8 ml of pH 6.3 ammonium acetate buffer / l seawater) across an 8-hydroxyquinoline column. This column cleaned seawater was acidified shortly after collection either for carrier use (see next section) or standard preparation.

Carriers: Fe carrier was prepared by adding 24 ml of 6M HCl to 1 l of column cleaned seawater. Al carrier was prepared by adding 8 ml of 6M HCl to 1 l of column cleaned seawater.

Standards: mixed Al/Fe stock standards (18 μM Al, 1 μM Fe) were prepared by the addition of known amounts of commercial Al and Fe stock standards (Fisher Scientific Certified Reference Solution) to acidified DI. Working standards were prepared each day by spiking appropriate amounts of stock standard to acidified (1 ml 6M HCl/l), 0.2μm-filtered seawater.

2.2.2. Experimental

The incoming filtered surface seawater from the fish flowing at 2.5 ml/min was acidified in-line with 0.15N HCl flowing at 0.1 ml/min which gives a final acid
concentration of 1 ml 6N HCl/I in the sample line, the same acid concentration as the standards. The acidified surface seawater was continuously pumped into a small polyethylene vial (0.5 ml capacity) mounted within a 50 ml polycarbonate centrifuge tube outfitted with an overflow system. This simple design was developed to eliminate the problems of outgassing when cold surface seawater is pumped into a warm laboratory (Vink et al., 2000). Into the smaller 0.5 ml capacity polyethylene vial were drilled two small holes. The first is for the sample inlet coming from the fish line tubing and the second is for the sample outlet being pumped to the FIA system. In addition to solving the outgassing problem of cold surface water, this technique provides a simple solution to the problem of equalizing flow rates between the sample being pumped in from the fish line and sample being pumped out to the FIA.

2.2.3. Fe Determinations

Fe determinations were made using in-line preconcentration and spectrophotometric detection (Rainin Dynamax UV-C). This method (Measures et al., 1995) utilizes in-line preconcentration of Fe onto a column of resin-immobilized 8-hydroxyquinoline along with the batch-spectrophotometric method of Hirayama and Unohara (1988). Briefly, an acidified seawater sample, buffered in-line to pH 5.5 with 2M ammonium acetate buffer (pH 6.3±0.1), was pumped through a 6-port 2-position valve (Valco Cheminert) across a 2 cm 8-HQ column for a specified time (e.g., 1min),
allowing for absorption onto the column of Fe in the sample. The valve is then switched back to the inject mode and an acid carrier flows across the 8-HQ column in the reverse direction, desorbing Fe from the column. The carrier stream then mixes into the reagent stream consisting of 3.5 mM DPD, 0.18M hydrogen peroxide, and the 2M ammonium acetate reaction buffer. The reaction mixture passes through a 0.5m knitted tubing coil heated at 30°C and is pumped into the spectrophotometer.

Fe was determined by the spectrophotometric detection of DPDQ, the semiquinone oxidation product of DPD. This oxidation is generated by hydrogen peroxide in the presence of Fe. Standardization was achieved by periodically switching from the fish line to lines placed in bottles containing working mixed Al/Fe standards using a sample distribution valve (Valco 8-port Cheminert).

The detection limit of the method can be estimated from the standard deviation of a low concentration iron sample. A 0.49 nM iron sample had a standard deviation of 0.03 nM and a relative standard deviation of 6.1%. Assuming the detection limit is three times the standard deviation of the low Fe sample, this implies a detection limit of 90 pM Fe.

2.2.4. Al Determinations

Al determinations were made using the fluorometric method of Resing and Measures (1994). The FIA-Al method also employs in-line preconcentration onto a
column of resin-immobilized 8-hydroxyquinoline but uses fluorometric detection (Rainin Model FL-1 Fluorescence Detector). The sample outlet from the 6-port Fe valve is the sample inlet to the 6-port Al valve. The buffered seawater sample (pH 5.5) is again pumped through a 6-port 2-position valve (Valco Cheminert) across a 7 cm 8-HQ column for a specified time, allowing for absorption of Al in the sample onto the column. Once the valve is switched back to the inject mode acid carrier (8 ml 6M HCl/l) flows across the column in the reverse direction and desorbs Al from the column. The carrier stream mixes with the lumogallion/buffer reagent and then passes through a 2-m knitted Teflon coil heated to 50°C. Brij-35, a micelle-forming detergent, is added to the carrier/lumogallion stream before it enters the spectrofluorometer, enhancing the sensitivity of the method by a factor of 5.

Al is determined by the fluorometric detection of the lumogallion-Al complex. Standardization is achieved by periodically switching from the fish line to lines placed in bottles containing working mixed Al/Fe standards using a sample distribution valve (Valco 8-port Cheminert).

Again assuming a detection limit based on three times the standard deviation of a low-concentration Al sample, a 1.0 nM Al sample yielded a standard deviation of 0.05 nM and a relative standard deviation of 5.0%. This implies a detection limit of 0.15 nM Al.
The Fe-Al FIA system was automated, alternating between Fe and Al every three minutes when using a one-minute load time (preconcentration) and longer for extended load times. During transects of the cruise where Al and Fe concentrations became relatively low (e.g. < 1nM Al and/or < 0.5 nM Fe) three minute load times were used. Usually, for a 1-minute load time, two underway runs consisting of 21 samples each were followed by a set of Al and Fe mixed standards. For a one minute load time, one sample could be run in 4 minutes. Thus, 21 samples were run over roughly 1.5 hrs. So, in all, 42 samples would be run over a course of 3 hrs and then a set of standards would be run over the next 1/2 hr. For a three-minute load time, one underway run consisting of 21 samples was followed by a set of Al and Fe mixed standards. For a 3-minute load time, one sample could be run in 8 minutes. Thus, 21 samples were run over roughly three hours and then a set of standards would be run over the next hour. So, for 1-minute and 3-minute loads, standards were run approximately every three hours. Typical Al/Fe detector outputs for a 1-min load standard run are seen in Figure 2.2. The corresponding Al/Fe standard curves from the data output in Figure 2.2 can be seen in Figure 2.3.

2.2.5. Blanks

Sample buffer and fish acid blanks were determined usually twice daily or when a new batch of reagents and/or fish acid was prepared. Three 125 ml aliquots of 0.2µm filtered surface seawater were collected in 125 ml bottles. 125 µl 6M HCl was added to
each aliquot. To the sample buffer blank was added an additional 125 µl 6M HCl and 5 ml sample buffer. To the fish acid blank was added simply an additional 5 ml of the 0.15M HCl fish acid. The sample buffer blank, the fish acid blank, and the "+0" blank sample were ran for Al and Fe. The value of the sample buffer blank, if any, was the sample buffer blank concentration minus the "+0" blank concentration. Likewise, the value of the fish acid blank, if any, was the fish acid blank concentration minus the "+0" blank concentration.

The values of the sample buffer blank and fish acid blank indicate the Al/Fe contribution that the in-line sample buffer and in-line fish acid (for in-line sample acidification) contribute to the overall sample concentrations. Any Al or Fe blank contribution from either the fish acid or sample buffer was calculated and subtracted from the sample values during data reduction.

2.3. Ancillary Measurements

Three times daily, discrete underway samples were collected from the towed fish sample outlet for the determination of salinity and nutrients. The salinity samples were analyzed on board using a calibrated Autosal salinometer and the nutrient samples were analyzed at the Univ. of Hawaii using a Technicon Autoanalyzer (Morse, pers. comm.).

In addition, conductivity and temperature were recorded every minute using probes in the ship's seawater intake line. These values were recorded along with the
ship’s position on the shipboard computer. Comparison of the discrete samples analyzed on-board and the ships underway salinity records indicate good agreement within ±2%.

2.4. Fe and Al Data Reduction

Shipboard data was separated into daily logs for each day of the cruise. Raw Al and Fe concentrations were calculated using the slope of the respective standard curve. Al and Fe sample concentrations were determined by dividing the Al and Fe detector output peak heights by the slope of the respective standard curve. If significant drift had occurred during the day’s runs in the slope of the standard curve then the raw data was drift corrected using a Kaleidograph drift-correction macro. The Kaleidograph macro assumes the first slope given is correct and notes the difference in following slopes. The macro numerically corrects for the difference in the following slopes relative to the first slope of the first standard curve. For instance, if the second slope is significantly lower than the first slope, the macro will raise the values of the samples run in between the first set of standards and second set of standards.

In some instances, possibly due to carryover of Fe on the column within duplicate runs of the same working standard, the peak heights of duplicates of the same standard were significantly different (> 10%). If the Fe carryover problem was present throughout a day’s runs, the sample concentrations were not drift corrected. Instead, an average Fe standard curve slope was calculated for the day. Sample Fe concentrations
were then determined by dividing the sample peak heights by this average Fe standard
curve slope. Also, where applicable, the data were corrected for fish acid and/or reagent
blanks.

Data from samples contaminated due to changing of filters, pump tubing, or other
problems have been removed from the data set. For example, it was clear that after
running standards the first 2-4 Fe peak heights and first 1-2 Al heights were significantly
higher (>10%), due to sample carryover on the pre-concentration column. Thus, these
samples were removed from the data set. After bad data had been flagged and removed
from the data set, the time of each sample injection was determined from a log kept
during the cruise. Using this time and the estimated 3-minute residence time of the
surface water in the Teflon tubing before arrival at the FIA system, the time of sample
collection was determined. The 3-minute residence time of the surface water in the
Teflon tubing was determined by measuring the time for an air bubble to make its way
from the fish intake on the BT to the FIA sample inlet from the fish. Using the ship’s
underway log, the actual position of the ship at the time of sample collection was then
determined and Fe and Al concentrations were then matched with the ship's position.

Data from the continuous underway dissolved Al and Fe sampling were contoured
using Generic Mapping tools (Wessel and Smith, 1995). Contours were computed after
fitting a minimum curvature surface with tension to the gridded data (Smith and Wessel,
1990). Setting maximum tension in the surface grid constrains the solution so that local
maximum or minimum values occur only at points where there are data (Smith and Wessel, 1990).
Chapter 3: Results

In the following chapter, data collected from the 2002 IOC cruise are presented and described. In addition to the surface and deep-water Al and Fe concentrations, which are the main focus of this thesis, the ancillary parameter data (temperature, salinity, oxygen, and nutrients) are presented to provide a hydrographic background to aid in interpretation of the trace-metal data.

3.1. General Surface Water Description

The surface waters along the cruise track (Figure 1.4) can be divided into the warm, saline waters of the subtropical gyre south of ~34° N latitude and the colder, fresher waters of the subarctic gyre north of 42° N. The salinity differences between the two gyres can be easily explained by annual mean precipitation-evaporation (P-E) differences. P-E values of +50 cm yr\(^{-1}\) (freshwater gain) are found in the subarctic gyre while values less than -100 cm yr\(^{-1}\) (net evaporation) are observed in regions of the subtropical gyre (positive P-E values indicate freshwater gain; Oberhuber, 1988). Surface water temperature and salinity values (Figure 3.1) cover the range from the cold, fresh subarctic water profiles at St. 2 and 3 to the warm, saline waters evident in the subtropical gyre stations 6-9.
The subtropical and subarctic gyres are bounded by the Kuroshio and Oyashio Currents, respectively. The northward-flowing Kuroshio is opposed by the southward-flowing Oyashio. The separation point for the northward flowing Kuroshio is reached at ~ 34°N where a transition occurs from the northward-flowing Kuroshio proper to the eastward flowing Kuroshio extension. Similarly, the southward flowing Oyashio meets its separation point at ~ 42°N where it turns into the eastward flowing Oyashio extension (Subarctic Current).

The region between the Kuroshio and Oyashio is known as the mixed water region. Temperature and salinity here display the characteristics of a mixture of subarctic water and subtropical water. The injection of the Kuroshio and Oyashio extensions into the relatively quiet, open waters of the N. Pacific causes strong instability and convergence in the mixed water region (Tomczak and Godfrey, 1994). Numerous eddies and intrusions are usually found in this hydrographically dynamic locale.

3.2. Surface Water Ancillary Parameters

Temperature, salinity, and oxygen in the surface waters along the cruise track clearly display the hydrographic boundaries between the subarctic and subtropical gyres. The warm, saline waters (23-25 °C, 35.0-35.5) of the subtropical gyre clearly contrast the cold, low salinity waters (< 5 °C, 33.0-33.4) of the subarctic gyre (Figure 3.1). Highly-oxygenated surface water oxygen concentrations approaching 300 μmol/kg were
observed in the subarctic gyre due to the increased solubility of gases at the colder water temperatures observed there (Figure 3.2).

Nutrient concentrations along the cruise track (Morse, pers. comm.) clearly illustrate the high standing-stock of major nutrients in the western subarctic gyre in contrast to the oligotrophic subtropical gyre surface waters (Figure 3.3 and 3.4). Nitrate, phosphate, and silicate concentrations reached maximum values of 25 \( \mu M \), 1.5 \( \mu M \), and 45 \( \mu M \), respectively, in the cold, oxygen rich waters of the subarctic gyre. Nutrient concentrations showed sharp, decreasing gradients between the subarctic gyre and mixed water region. Subtropical gyre surface waters showed depleted nutrient concentrations with nitrate, phosphate, and silicate concentrations all below the respective detection limits (0.18 \( \mu M \) NO\(_3^–\), 0.70 \( \mu M \) Si(OH)\(_4\), 0.05 \( \mu M \) PO\(_4^{3–}\); based on 3 x std. deviation of a low nutrient sample).

3.3. Surface Al and Fe

Approximately 3300 underway surface dissolved Al and Fe determinations were made during the cruise (Figure 3.5). Minimum Al and Fe values of 0.2 nM and 0.1 nM, respectively, were observed near the edge of the subarctic gyre corresponding to decimal day 16.5 in Figure 3.5. Maximum Al and Fe values of > 30 nM and > 2 nM were observed just offshore of the Na Pali Coast of Kauai, corresponding to decimal day 30.0.
The surface Al and Fe concentrations have been gridded and contoured (see Sec. 2.4) to present a clearer geographical picture of concentration gradients along the cruise track (Figure 3.6). Fe concentrations were ~ 1nM in the mixed water region off Japan and fell to ~ 0.30 nM as the ship’s track crossed the mixed water region and reached the edge of the subarctic gyre. Subarctic gyre concentrations ranged from 0.15 nM to 0.50 nM with minimum Fe values found approaching St. 4. at the southern boundary of the subarctic gyre. As the ship moved through Stations 4, 5, and 6, Fe concentrations ranged from 0.25-0.40 nM with a slow increase observed as the ship moved further south into the subtropical gyre. Fe concentrations along the eastward transect in the subtropical gyre through Stations 8 and 9 were on the order of 0.50-0.75 nM and increased further to 1.0 nM as the ship track moved down the Northwest Hawaiian Island Chain. Northeast of the Hawaiian Islands Fe concentrations were ~ 0.50 nM.

Variability in Al concentrations along the cruise track (Figure 3.6) was somewhat similar to the changes observed in Fe. Mixed water region Al concentrations of 4 nM closer to Japan decreased through the mixed water region to < 2 nM at the edge of the subarctic gyre. Subarctic gyre Al concentrations ranged from < 0.3 nM to 2 nM with minimum values observed, similar to Fe, in the transect between Stations 3 and 4 at the southern edge of the subarctic gyre. Al concentrations of ~ 2 nM were observed along the transects between St. 4, 5, and 6 with an increase to ~ 4 nM observed approaching St. 7. Al concentrations of 3-4 nM in the subtropical gyre through St. 7-8 increased to > 6
nM as the ship track moved through the Northwest Hawaiian Islands. A significant Al maximum > 30 nM appeared just offshore of the Na Pali Coast of Kauai, indicative of a strong terrigenous input. Surface waters northeast of the Hawaiian Islands had Al concentrations of ~ 6 nM.

In summary, elevated Al and Fe concentrations were observed in the mixed water region closer to Japan. Al and Fe both decreased significantly as the ship moved through the mixed water region into subarctic gyre waters where the lowest Al and Fe concentrations were observed. Increased concentrations of Al and Fe were seen as the ship moved out of subarctic gyre waters, through the mixed water region, and into subtropical gyre waters. The maximum values of Al and Fe were observed in surface waters along the NW Hawaiian Islands.

Specific sections of the Al and Fe data presented in Figure 3.6 are plotted as individual data points along with temperature and salinity to provide a detailed look at the Al and Fe gradients observed in these regions.

3.3.1. Mixed Water Region of the Far Western Pacific

Values observed between Stations 1 and 2 (Figure 3.7) clearly show lower temperatures and salinities as the ship approached the colder, fresher waters of the subarctic N. Pacific gyre. The dynamic nature of this mixed water region is illustrated by
two large temperature and salinity minima (decimal day 9.3 and 10.4; Figure 3.7) indicative of cold-core rings likely shed off the Oyashio Extension (Subarctic Current).

Al and Fe both display overall decreasing trends through the mixed water region heading northeast towards St. 2 (Figure 3.7). Al concentrations decrease from ~ 4.5 nM in the mixed water region at decimal day 8.45 to 0.5 nM in the subarctic gyre at decimal day 11.0. However, in the midst of this decrease a local Al increase is observed (Figure 3.8) at decimal day 9.1 from 1 nM to 2.5 nM Al. This local increase is coincident with a local minimum in sigma theta possibly indicating subtropical gyre water and elevated levels of Al (Figure 3.8).

Fe concentrations decrease five-fold from 1 nM to 0.2 nM between decimal day 8.5 (35°N, 140°E) and decimal day 11.0 (42°N, 153° E ; Figure 3.7). There does appear to be a slight local maximum of 1.1 nM Fe at decimal day 8.8-8.9. This Fe maximum is defined by a very smooth maximum in SST and salinity which could indicate entrainment of higher Fe-subtropical gyre water in the mixed water region.

3.3.2. Subarctic Gyre

Interestingly, within subarctic gyre waters, while temperatures (2.5-4°C) and salinity (32.9-33.1) are fairly uniform, Al and Fe show significant variation (Figure 3.9). The gaps in ancillary data are due to flow problems in the ship's underway surface pump.
Al values of ~ 0.4 nM increase dramatically between St. 2 and St. 3 to ~ 2 nM before slowly returning to 1 nM approaching St. 3. The southward transect from St. 3 towards St. 4 shows relatively uniform Al concentrations of ~ 0.5 nM. It is also noted that the Al concentrations coming out of St. 3 (~ 0.5 nM) are somewhat lower than those observed coming into Station 3 (~ 1 nM).

Fe concentrations range from a maximum of ~ 0.6 nM soon after departure from St. 2 to a minimum of ~ 0.1 nM on the southward transect towards St. 4. A slight Fe increase to 0.50 nM is observed at decimal day 16.1. It should also be noted that Fe data from decimal day 12.8-13.5 have been discarded. It was concluded that these values were erroneously high due to non-replacement of the in-line 0.45 μM filter while at St. 2. Thus, the samples collected upon leaving Station 2 were contaminated with Fe leached from particulate material on the filter.

3.3.3. Mixed Water Region Heading South

Temperature and salinity both begin to increase significantly at decimal day 16.8 (45.2°N, 170.6°E) indicating the passage of the ship out of the subarctic gyre and into waters of the northern mixed water region (Figure 3.10). During the southern transit from 46.6°N to 30.9°N latitude along 170.6°E (dec. day 16-22), the surface temperature and salinity increased from 3.5 °C and 33.0 to 19°C and 34.7, respectively.
Over this same region Al and Fe increase slightly from 0.5 nM and 0.20 nM, respectively, at 46.6°N latitude to ~3.5 nM and 0.35 nM at 30.9°N latitude (Figure 3.10). The increase in both Al and Fe values coming onto St. 4 at decimal day 17.9-18.0 and the increased values upon station departure are also worth noting. Al and Fe values increased from 0.5 nM and 0.1 nM, respectively, to 2 nM and 0.2 nM just before arrival at St. 4. These values upon station departure showed further increases. It is possible that these Al and Fe increases are due to the ship’s passage across an eddy of subtropical origin in the mixed water region near St. 4. Salinity and temperature data trends are consistent with an increasing influence of subtropical gyre water during this station's occupation. Finally, temperature and salinity data during decimal day 19.5-20.2, although sparse, indicate stable values of 18.8°C and 34.8. This was thought to be representative of Kuroshio extension waters and it was presumed that the occupation of Station 5 took place within the Kuroshio extension.

3.3.4. Subtropical Gyre Waters Heading East Towards Hawaii

The eastward transit through the subtropical gyre between Stations 7,8, and 9 showed surface temperatures ranging from 24-26°C and salinities of 34.8-35.5 (Figure 3.11). Salinity remained very uniform until decimal day 28.0 when a slow decrease started to occur, coincident with the observation of rainfall as the ship approached the Hawaiian Islands.
Al concentrations along the same eastward transit (Figure 3.11) were fairly constant at 3-5 nM until decimal day 30.0 when significant increases occurred. Al values increased to > 20 nM as the ship approached the Na Pali Coast of Kauai with values just offshore reaching 50 nM. It is worth noting that the Al scale in Figure 3.11 only reaches 20 nM in order to provide greater resolution.

Fe concentrations, in contrast, are more variable and sporadic over short distances along this transect of the cruise (Figure 3.11). Fe ranged from 0.4 nM to > 1 nM but with significant increases and decreases over periods of hours. For example, Fe increases from 0.6 nM to 1.2 nM over a half-day period from decimal day 27.5 to 28.5. These changes illustrate the likely "biogeochemical patchiness" of this biologically-required trace element (higher productivity areas with lower [Fe]) or possibly an enrichment of Fe due to island effects. Maximum Fe values approaching 2 nM were also observed off the Na Pali Coast.

3.3.5. Surface Water Al and Fe Summary

The overall pattern of Al distributions was of higher values at lower latitudes in subtropical gyre waters and lower values in high latitude subarctic gyre waters of the N. Pacific. In addition, surface Al concentrations generally seemed to be higher in the central N. Pacific subtropical gyre than in the western subtropical gyre.
Fe concentrations showed somewhat similar trends (albeit with notable exceptions) with low values in the northern subarctic gyre waters and increasing Fe values as the ship moved into subtropical gyre waters closer to the Hawaiian Islands.

Discussion of the surface Al and Fe trends in the next chapter will focus on input by atmospheric dust deposition and the effects of the seasonal removal of Fe by biological processes. In addition, NO$_3^-$:Fe ratios will be examined along the cruise track to examine biological limitation by Fe in the central and western N. Pacific.

3.4. General Intermediate and Deep Water Hydrography

The surface salinities of the N. Pacific are much lower than those in the N. Atlantic and, thus, the surface densities in the N. Pacific are too low to allow for the formation of deep or bottom water.

Instead, the deep and bottom waters of the N. Pacific are formed in the N. Atlantic and Weddell Sea through thermohaline convection and are known respectively as North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW). Antarctic Bottom Water slowly advects into the N. Pacific filling the basin below 3000 m from the south (Tomczak and Godfrey, 1994).

Water in the depth range of 1000-3000 m is not produced through active circulation but, rather, the water properties are determined by complex mixing processes. This water is known as Pacific Deep Water and consists of Antarctic Bottom Water,
North Atlantic Deep Water, and Antarctic Intermediate Water. The contribution of NADW to Pacific Deep Water is indicated by a salinity maximum near 3000 m depth in the S. Pacific (Tomczak and Godfrey, 1994). This salinity maximum can be followed just north of the equator. Further north, the gradual extinction of NADW occurs as Pacific Deep Water is formed.

Although the surface salinities of the N. Pacific are too low to prevent deep and bottom water formation, the low temperature and salinity of surface waters in the subarctic gyre do allow for intermediate waters to be formed. North Pacific Intermediate Water (NPIW) is formed at the boundary between the mixed water region and subarctic gyre known as the Polar Front. Here low salinity subarctic gyre surface water mixes with deeper waters and is subducted into the subtropical gyre south of ~ 40°N, forming the salinity minimum intermediate water of the subtropical gyre. This NPIW spreads just below the permanent thermocline and moves equatorward along isopycnal surfaces at 300-800 m depths (Tomczak and Godfrey, 1994).

Above the NPIW, the water masses of the thermocline and surface layer in the N. Pacific are generally known as North Pacific Central Water as they cover a broad range of T-S values (7-20°C, 34.1-34.8). This Central Water is produced during subduction at the Subtropical Convergence Zone in late fall and winter (Tomczak and Godfrey, 1994). The North Pacific Central Waters can be broken down into Western North Pacific Central Water (WNPCW) and Eastern North Pacific Central Water (ENPCW). A distinct
boundary between the two masses is found at $\sim 170^\circ$ W. ENPCW is fresher than WNPCW at temperatures below $17^\circ$C but more saline in the upper thermocline.

3.5. Hydrographic Setting of the Vertical Profile Stations

Potential temperature vs. salinity is plotted for each vertical profile station as well as for the underway surface transects between the stations (Figure 3.12). The T-S diagram shows the distinctive nature of the hydrographic regimes. Stations 1 and 5-9 show relatively warm, saline surface waters mixing into the salinity minimum at 600-800 m. Below this depth temperature decreases and salinity increases, respectively, to AABW values of 1.5°C and 34.7. Stations 2 and 3 are quite distinct with cold, low salinity surface waters increasing in salinity through the intermediate waters into the AABW. The T-S properties of surface waters observed between the stations cover the range of the subarctic, subtropical, and mixed water hydrographic regimes.

Temperature, salinity, and oxygen from the vertical profiles are presented as contour plots for the upper 1500 m of the water column along the cruise track (Figure 3.13). The plots clearly show the hydrographic boundaries of the subtropical gyre, subarctic gyre, and the mixed water regions between the two gyres as well as the formation and subduction of the low salinity Subarctic Intermediate Water. The temperature, salinity, and oxygen data were obtained from a Seabird 911 CTD attached to the rosette which was deployed at each station.
A sharp decrease in temperature between Stations 1 and 2 in the upper 500 m marks the boundary between the subarctic gyre, mixed water region, and the subtropical gyre. Subarctic gyre water temperatures range from 2-4°C with a subsurface minimum of ~1.5°C at the base of the winter mixed layer. At the boundary of the mixed water region (St. 4 and 5) temperatures in the upper 500 m increase dramatically. The subtropical gyre waters are characterized by uniform surface temperatures of ~24°C, a sharp thermocline in the upper 400 m, and intermediate water (500-1000 m) temperatures of 5-10°C.

The salinity contour plot shows a similar structure. Subarctic gyre salinities are characterized by an upper water (0-200 m) salinity minimum of ~33.0. Subtropical upper waters are significantly more saline with upper water values of ~35.2. Strong horizontal gradients in salinity are seen in the mixed water regions between Stations 1 and 2 and between Stations 4, 5, and 6. Low salinity NPIW is visible in the salinity contour plot at 500-1000 m in the subtropical gyre connected to the low salinity surface waters at the edge of the subarctic gyre.

Oxygen data along the cruise track shows a strong surface maximum of ~310 umol/kg in the cold surface waters of the subarctic gyre accompanied by a strong intermediate water minimum of ~30umol/kg underlying these waters (Figure 3.13). This strong oxygen minimum just below the well-oxygenated, low salinity subarctic gyre surface water is a result of the presence of the oldest water in terms of ventilation age in the world’s oceans (Tomczak and Godfrey, 1994). Horizontal and vertical gradients in
oxygen are present in the mixed water regions through Stations 4 and 5. Subtropical gyre water oxygen concentrations show a maximum in the surface waters of ~200 umol kg\(^{-1}\) and an oxygen minimum < 50 \(\mu\)mol kg\(^{-1}\) at ~ 1000 m.

Nutrient distribution represented by NO\(_3^-%) and SiO\(_2\) contours in the upper 1500 m along the IOC cruise track are shown (Figure 3.14). The most striking feature of the nutrient distributions are the upper water (0-200 m) maximum in the subarctic gyre region and detection limit nutrient values in the oligotrophic subtropical gyre. For example, NO\(_3^-%) concentrations at Station 3 in the upper 200 m approach 25 \(\mu\)M while corresponding concentrations in the subtropical region at St. 6-9 are below the detection limit of 0.18 \(\mu\)M.

In addition, the intermediate water (500-1000 m) nutrient concentrations are significantly higher in the subarctic region (St. 2 and 3) than in the subtropical gyre. Nitrate concentrations greater than 40 \(\mu\)M extend from deeper waters up to a depth of 250 m in the subarctic gyre. However, similar nitrate values only extend from deeper waters up to depths of ~1000 m in subtropical gyre waters. Silicate concentrations show a similar trend.
3.6. Vertical Profile Al and Fe Results

Total dissolved Al and Fe profiles are shown for Stations 1-9 in the upper 1500 m. In addition, station profiles of temperature, salinity, nitrate, and oxygen are shown for each station. The Al and Fe vertical profile stations are divided into groups based on the hydrographic regimes in which they were located. Stations 1, 4, and 5 were located in the Kuroshio and mixed water regions between the subarctic and subtropical gyres. Stations 2 and 3 were located in the subarctic gyre while Stations 6-9 were located in the subtropical gyre.

3.6.1. The Subarctic Gyre Stations

The surface waters at Stations 2 and 3 (Figure 3.1) clearly show the low salinity (< 33.5), low temperature (2-4°C) waters characteristic of the N. Pacific subarctic gyre. Surface densities (\(\sigma_s\)) in the region range from 26.0 - 26.4 and mixed layers of 55 m and 110 m at Stations 2 and 3, respectively, were observed. The base of the mixed layer was defined as the depth where the in-situ density (\(\sigma_s\)) differed from that of the surface by at least 0.125 kg m\(^{-3}\). At these stations surface waters were rich in both macronutrients and oxygen.

Temperature, salinity, nitrate, and oxygen profiles are shown for both Stations 2 and 3 to aid in Al and Fe data interpretation (Figure 3.15). Deep winter mixing down to a depth of ~ 110 m is indicated at Stations 2 and 3 by the temperature profile below the
seasonally warmed mixed layer. At both stations the temperature minimum at 110 m indicates the base of the winter mixed layer. At this depth NO$_3^-$ concentrations were 23.7 uM and 24.5 uM at Stations 2 and 3, respectively (Figure 3.15). These concentrations are likely indicative of surface winter nitrate values in the region.

Surface mixed layer Al values at St. 2 and 3 were fairly consistent at ~ 1 nM while Fe values were 0.6 nM at St. 2 and 0.3 nM at St. 3 (Figure 3.16). Below the deep winter mixed layer salinity increases significantly and oxygen values decrease rapidly to values less than 50 $\mu$mol kg$^{-1}$ at 250 m (Figure 3.15). This oxygen minimum is evident in the water column down to 1200 m at both Stations 2 and 3 and appears to coincide with increases in Fe to ~ 1.3 nM over the same depth range. Al values in the oxygen minimum remain fairly uniform at Station 2 at ~ 1 nM but increase from ~ 1 nM to 3 nM at Station 3. Intermediate water Al values (1200-1500 m) were ~ 1 nM at Station 2 yet significantly higher at Station 3, ranging from 3-5 nM. Fe values over the same intermediate depth range show significant variability with 0.6-1.2 nM Fe at Station 2 and 1.0-1.5 nM Fe at Station 3.

3.6.2. Mixed Water Region Stations

Stations 1, 4, and 5 are grouped together as occupying the Kuroshio waters of the mixed water region between the Kuroshio and Oyashio. Surface water temperatures in both the western mixed water region between Stations 1 and 2 and the central mixed
water region near Stations 4 and 5 range from ~ 10°C to 20°C. Surface water salinities as low as 33.8 were found in northern mixed water region waters closer to the Polar Front and increased to ~ 34.5 closer to the subtropical gyre.

Intrusions in the temperature, salinity, and oxygen profiles indicate the dynamic nature of the mixed water region (Figure 3.17). Station 1 profiles show a low salinity, low temperature, high oxygen intrusion at 450 m depth, likely indicative of subarctic gyre surface water entrained in the mixed water region. A second, similar intrusion is seen at 700 m depth.

At Stations 4 and 5 salinity minimum water (~ 33.8 °C) is seen at 200 m and 750 m, respectively (Figure 3.17). The salinity minimum at Station 4 is at a potential density (σθ) of 26.38-26.49 while the minimum at Station 5 lies on the 26.76-26.86 isopycnal, encompassing the density surface of NPIW centered on the 26.8 isopycnal surface (Qui, 1995).

Surface mixed layer Al and Fe were ~ 3 nM and 0.5 nM, respectively, at Stations 1 and 5 (Figure 3.18) with Al showing a significant increase at 250 m at both stations. Al increases to 9 nM at Station 1 and 5 nM at Station 5. Interestingly, Al at Station 4 only shows a slight 1 nM increase over this depth range while Fe increases from 0.7 nM to 0.9 nM at 125-250 m depth. Fe showed no concentration change over the depth range of the Al maximum at either St. 1 or 5.
Potential density ($\sigma_\theta$) over the 150-300 m depth range, the location of the Al maximum, was 25.0-25.6 and 25.30-25.74 at Stations 1 and 5, respectively, indicating that the source of this Al maximum is likely the same at both stations. However, Station 4 central water densities ($\sigma_\theta$) at the location of the Fe maximum were 26.37-26.57, indicating that the likely source of the Al maximum at Stations 1 and 5 is not the same as the Fe maximum source at Station 4.

Deep water Al values were fairly uniform in the mixed water region at 1-3 nM. Deep water Fe values, however, display significant differences. Fe concentrations at 1000-1500 m depth at St. 4 and 5 were ~ 0.5 nM. Fe concentrations at similar depths at Station 1, however, were ~ 2 nM. While these higher Fe values may reflect the closer proximity of Station 1 to the Japanese coast, it should be noted that the deep sampling at St. 1 was the first use of the Go-Flo bottles and the St. 1 deep water Fe values could possibly be higher due to contamination from the bottles.

3.6.3. Subtropical Gyre Stations

The warm, saline surface waters of the subtropical gyre characterized the transects between St. 6 and St. 9 (Figure 3.1). Surface water temperatures were in the range of 22°-27°C and surface water salinities of 34.7-35.5 were observed. Relatively shallow surface mixed layer depths were observed of ~ 30 m at St. 6 and 7 and ~ 20 m at Stations 8 and 9.
Upper waters (0-250 m) display uniform oxygen concentrations of ~ 200 μmol/kg (Figures 3.19 and 3.20). Oxygen concentrations at St. 6-9 decrease from 300-750 m reaching a minimum (< 50 μmol kg⁻¹) at 750-1000 m depth. Salinity profiles at all the subtropical gyre stations show a salinity minimum at 500-600 m indicative of the North Pacific Intermediate Water formed and subducted at the Polar Front.

Surface mixed layer Al ranges from 4-6 nM with no clear geographic pattern. Surface mixed layer Fe, however, shows a steady increase from 0.4 nM at St. 6 to almost 1 nM at Station 9 as the ship moved east (Figure 3.21).

A subsurface Al maximum (150-300 m) was observed at St. 6 and 7 with Al values of ~ 6 nM. Potential densities over the depth range of this maximum were 25.43-25.70 and 25.35-25.55, respectively, similar to those of the Al maximum observed at Stations 4 and 5. An equivalent feature is not observed in the Fe data.

In deeper waters Al decreases from the subsurface maximum to uniform values of ~ 2 nM at 1500 m for St. 6-9. However, the same geographic pattern of increased Fe surface values from west to east is also observed in deeper (500-1500 m) waters as well with values at 1500 m increasing from 0.6 nM at St. 6 to 1.2 nM at Station 9.

3.6.4. Vertical Profile Al and Fe Summary

While each particular station showed specific trends with respect to Al and Fe, several features merit further discussion. First, the well-defined subsurface Al maximum

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m at Stations 1, 5, 6, and 7 is worth investigating. It was observed that this Al maximum at each of the stations lies on a very similar density surface (25.2-25.6). It is possible that the source of this Al maximum might be due to outcropping of a surface water in an elevated dust input regions or the advection of coastal waters high in Al.

Second, the Fe increase at the subarctic gyre Stations 2 and 3 coincident with the upper water oxygen minimum implies, perhaps, an increased Fe solubility with decreased oxygen concentrations or remobilization of organic matter. Third, the observed increase in both surface and deep water Fe concentrations through St. 6-9 might reflect a similar geographic gradient in atmospheric dust deposition. Finally, Al profile behavior implies increased deposition in the central subtropical gyre. Nutrient-like profiles are observed in the subarctic gyre and mixed water region while increased surface levels of Al and scavenging with depth are observed at subtropical gyre Stations 8 and 9.

The features described above are likely tied to variations in the inputs, especially atmospheric dust deposition, and geochemical cycling of Al and Fe in the Pacific basin. Thus, a discussion of the causes and features of these effects will be given in the next chapter.
Chapter 4: Discussion

The surface and deep-water Al and Fe distributions presented in the previous chapter can be interpreted in terms of their supply and removal. As previously stated, in an open-ocean environment such as the western and central N. Pacific, atmospheric dust deposition is the primary external source of reactive trace metals to surface waters. Once deposited in the surface waters a biologically-required element such as Fe will undergo a complex euphotic zone cycling of biological uptake, biogenic remineralization, and active particle scavenging. In contrast, Al does not undergo active biological uptake but is passively scavenged on particle surfaces and leaves the photic zone. Variations in these input and removal processes of Al and Fe lead to their regional variations in concentration. The focus of this chapter is to interpret the Al and Fe data in terms of atmospheric deposition estimates, biological limitation, and deep-water traces of eolian inputs.

4.1. Comparison with Previous Data

Previous Al and Fe data from the western and central N. Pacific are consistent with the surface and deep-water distributions presented here. At the VERTEX-IV station (28°N, 155°W) during July, 1983, Orians and Bruland (1986) found dissolved Al surface mixed layer concentrations of 5.0 nM, a sharp decrease through the thermocline to values
of 1.0-1.5 nM at 100-300 m, and a decrease to ~ 0.4 nM at 800-2000 m. The 2002 IOC data at Station 9 (ALOHA; 22° N, 158° W) show similar surface mixed layer values but slightly elevated intermediate and deep water values. Orians and Bruland (1986) indicate increased scavenging with the age of the water mass leading to the lower Al values in intermediate and deeper waters of the N. Pacific. Dissolved Al in the Weddell Sea (Moran et al., 1992), an area characterized by low atmospheric dust input, showed surface values of 4-5 nM and a decrease to 2 nM at 1500 m depth.

The 2002 IOC dissolved Fe data seem to be consistent with existing data in the N. Pacific subarctic gyre and less so with subtropical gyre Fe data. Nakabayashi et al. (2002) sampled surface and upper waters (0-250 m) inside and outside a high-production spring bloom patch at 44.0-44.8°N and 154.8°-156.3°E, the same location as Station 2 (KNOT). Surface mixed layer concentrations range from 0.20 nM -0.40 nM both inside and outside the patch with deeper water (150-250 m) values > 1 nM. 2002 IOC Station 2 mixed layer values were ~ 0.60 nM while 150-250 m values were 0.7-1.2 nM. Fujishima et al. (2001) found Fe surface values from below detection limits ( < 0.28 nM) to 0.50 nM and deep water values of 0.5 nM-1.1 nM in waters of the western subarctic N. Pacific.

In N. Pacific subtropical gyre waters near Hawaii, Wu et al. (2001) observed 0.5-0.7 nM Fe in surface mixed layer waters, a 0.2 nM minimum at 350 m, and an increase with depth to 0.7 nM at 1500 m depth. At VERTEX-IV (see above) Bruland et al. (1994)
report surface water values of 0.37 nM, a sharp decrease through the seasonal thermocline to values of 0.02 nM at 100 m, and a further gradual increase with depth to values of 0.45 nM at 1000 m. In comparison, subtropical IOC stations reveal surface water values > 0.60 nM Fe and deeper waters in excess of 1 nM.

4.2. MADCOW Model Dust Deposition Estimates

The underway surface Al data can be used as a proxy for estimating dust deposition to the surface waters of the N. Pacific. As mentioned in Chapter 1, the Duce model dust flux estimates yield significant inputs of mineral dust to the surface waters of the far western N. Pacific in excess of 10 g m\(^{-2}\) yr\(^{-1}\) (Figure 1.2).

The MADCOW model was applied to the surface water Al data presented in the previous chapter in order to compare the results with the Duce model. Figure 4.1 is a contour map of model-derived dust estimates for the 2002 IOC cruise track. The model dust flux estimates were calculated using a 5 year residence time for Al and a mathematical mean of the 1.5% to 5% dust solubility range observed in laboratory experiments.

Instead of the MADCOW uniform mixed layer depth of 30 m, a variable mixed layer depth based on station observations was used. For example, subarctic gyre mixed layer depths at Stations 2 and 3 were on the order of 60 m and 110 m, respectively, using 0.125 kg m\(^{-3}\) criteria. An iterative process was used to calculate mixed layer depth for
each transect of the cruise track. For example, surface dust flux estimates upon leaving St. 2 were calculated using a mixed layer depth of 60 m. The mixed layer depth was assumed to increase linearly along the cruise track to the 110 m observed at Station 3. Although this linear increase is likely a simplification, it is a more accurate approach than assuming a uniform 30 m mixed layer depth for the entire cruise track. In a similar manner, mixed layer depths were calculated for the other sections of the cruise track. The mixed layer depth ranges for each transect of the cruise track are shown in Table 4.1.

The results of this calculation show model dust estimates ranging from 0.03 g m\(^{-2}\) yr\(^{-1}\) in the subarctic N. Pacific to > 2 g m\(^{-2}\) yr\(^{-1}\) near the Hawaiian Islands. The highest estimates found just offshore of Kauai are presumably due to local run-off and not atmospheric deposition. In general, ignoring these coastal waters, the largest MADCOW dust estimates (~0.4-0.5 g m\(^{-2}\) yr\(^{-1}\)) were observed in the subtropical gyre between Stations 7 and 8. The lowest values (~0.05 g m\(^{-2}\) yr\(^{-1}\)) were observed in the subarctic gyre, along the transect between Stations 3 and 4.

It is quite obvious by comparing the 2002 IOC Al-derived dust estimates with the Duce model that there are significant differences between the two. The Duce model predicts significantly higher dust inputs to the waters of the western and central N. Pacific. In the far western N. Pacific where the Duce model predicts a dust flux of > 10 g m\(^{-2}\) yr\(^{-1}\) while the largest surface water Al-derived estimates are less than 1 g m\(^{-2}\) yr\(^{-1}\). Similarly, in the area estimated by Duce et. al (1991) to have 1-10 g m\(^{-2}\) yr\(^{-1}\) of mineral
dust flux, the largest surface water Al-derived dust estimates seen are on the order of 0.50 g m\(^{-2}\) yr\(^{-1}\). The 2002 IOC results also indicate that the geographical pattern of dust deposition in the N. Pacific is distinct from the Duce model. The Al-derived dust fluxes appear to increase with distance from Asia moving from west to east in the N. Pacific. In contrast, the Duce model shows increased dust fluxes closer to Asia and decreasing fluxes as one moves east towards the Central Pacific and the Hawaiian Islands.

It is quite likely that the Duce model is over-estimating fluxes of mineral dust to the surface waters of the central and western N. Pacific. It is well-understood that dust production, transport, and deposition processes are all highly episodic and associated with the propagation of dust storms (Uematsu et al., 1983). Long-range dust transport requires the rapid movement of dust to high altitudes, often up to between 1 and 5 km in the Atlantic and 6-8 km in the Pacific (Prospero, 1995; Prospero, 1989). Due to this high-altitude atmospheric transport, dust concentrations measured at the Cape Verde Islands off the North African coast are not exceptionally high despite lying directly underneath of the major Saharan dust plumes (Chiapello et al., 1995). This is due to the fact that the dust is travelling above the marine boundary layer and only wet deposition (rainfall) would allow for dust to reach the ocean surface from such altitudes.

It is highly likely that the differences between the Duce model and the Al-based surface dust flux estimates to the northwest Pacific ocean are largely due to the high-
altitude transport phenomenon. The dust simply is not being deposited although it is
being transported directly over the study area at high altitude.

4.3. Fe Limitation in the Western Subarctic N. Pacific

It is worth examining the fluxes of dissolved Fe to surface waters with regard to
biological Fe limitation in the N. Pacific. Atmospheric deposition of Fe and upwelling of
Fe associated with sub-surface waters are the principal sources of Fe to surface waters of
the region. It is possible to compare the relative importance of the upwelled supply of Fe
to that from atmospheric deposition through its ratio to NO$_3^-$ (Measures and Vink, 1999).

Sunda and Hunstman (1995) proposed that systems are Fe-limited if the C:Fe
ratio in the organism exceeds $10^5:1$ and Fe-replete if the C:Fe ratio is less than $10^5:1$. Using the Redfield C:N ratio of 6.63 it can then be calculated that systems become Fe­
limited systems if the N:Fe ratio is $> 15,000:1$; Fe-replete systems will have N:Fe $<$
15,000:1.

Inspection of the surface water values clearly shows dramatically elevated N:Fe
ratios in waters of the subarctic gyre (Figure 4.2). Based on temperature and oxygen
profiles at subarctic gyre St. 2 and 3, it is estimated that deep winter mixing in these
regions occurs down to depths of $\sim$ 110 m (Figure 3.15). Thus, it is estimated that the
upwelled water due to deep winter mixing in the subarctic gyre will have characteristics
similar to the water at 110 m. Based on samples collected at 60 m, 80 m, and 100 m at
Stations 2 and 3, N:Fe ratios of 30,000-44,000 and 65,000-87,000 are observed, respectively -- both well above the N:Fe biological limitation threshold. Thus, it is estimated that the upwelled water in the subarctic gyre will have a Fe concentration of ~ 0.5 nM and a N:Fe ratio of 40,000-90,000.

Maximum atmospheric dust flux estimates, assuming 1.5% Al partial solubility, to the subarctic region based on surface water Al concentrations are ~ 0.50 g m\(^{-2}\) yr\(^{-1}\). Assuming an average mineral aerosol content of 1 mmol Fe g\(^{-1}\) dust (Wedepohl, 1995), a 1.5-5% partial solubility (similar to Al), and a 50 m mixed layer, an additional 0.15-0.5 nM Fe will be supplied per year by atmospheric dust input.

Combining this atmospheric input with the maximum 0.70 nM Fe observed in deep mixed water of the subarctic gyre yields a total maximum 0.85-1.2 nM Fe in the surface waters of the subarctic N. Pacific. Using a mean deep mixed water NO\(_3\) concentration of 22.5 µM, the maximum and minimum N:Fe ratio in the surface waters range from 18,750:1 to 26,470:1, all indicative of Fe limitation.

It is worth noting that if deep mixing did reach the 250-750 m subarctic oxygen minimum, Fe supplies to the surface waters via upwelling would be on the order of ~ 1.2 nM. This magnitude of Fe supply in combination with the observed atmospheric Fe input would decrease the ratio of N:Fe to ~ 12,000:1, well into the Fe-replete range.

It should be mentioned that the above calculations significantly simplify the complex dynamics of Fe input, uptake, and removal but, nevertheless, provide useful
boundary calculations. These calculations do show, for example, that the amounts of Fe supplied by upwelling and atmospheric input are insufficient to allow for complete removal of the accompanying nitrate and its export production in the subarctic N. Pacific. In order to remove 23 μM NO$_3$ from the surface waters, ~ 1.5 nM Fe is necessary while roughly less than half of this Fe is available in subarctic N. Pacific surface waters.

4.4. Al and Fe Depth Profile Features

With regard to the vertical distributions of Al and Fe observed during the 2002 IOC cruise, there are three features that will be discussed. The first is the significant Fe increase coincident with the sharp oxygen minimum in subarctic gyre waters. The second is the Fe increase in both surface and deep water as the ship's track moved eastward towards the Hawaiian Islands. Finally, the Al subsurface maximum will be discussed in terms of possible sources.

4.4.1. Fe at the Oxygen Minimum in the Subarctic N. Pacific

A broad, sharp oxygen minimum (~ < 50 μmol/kg) was observed in the subarctic gyre Stations 2 and 3 between 250 m and 1000 m, coincident with an increase in Fe concentrations from 0.5 nM in surface waters to ~ 1.2 nM at 250 m. Landing and Bruland (1987) observed similar Fe increases from 0.3 nM Fe surface waters to ~ 2 nM Fe in suboxic conditions at 100-400 nM at VERTEX-II in the Eastern Tropical North
Pacific. This increased dissolved Fe at the oxygen minimum either results from an in-situ reduction of Fe to a more soluble form [Fe(II)] or simply from a greater vertical flux of particulate material and its subsequent remobilization leading to enhanced steady-state Fe levels.

The consumption of oxygen in oxygen-minimum regions is due to oxidation of organic matter. Under low oxygen conditions, organic matter oxidation will continue to occur with nitrate serving as the primary electron acceptor. The redox chemistry of the trace species Mn, Cr, and Se has been shown to be influenced by oxidation-reduction processes in oxygen-minimum zones (Rue et al., 1997). For example, Mn in suboxic regions undergoes reductive particle dissolution, displaying a significant increase in the dissolved fraction.

Contrary to Mn, Fe has been shown not to be reduced in situ from settling particles in suboxic regions. Landing and Bruland (1987) measured dissolved and particulate iron fractions in the oxygen minimum at VERTEX-II and concluded that the observed dissolved Fe maximum was the result of horizontal transport. In addition, it was shown that anoxic conditions are necessary for the reductive dissolution of inorganic particulate iron. Thus, in the NW subarctic Pacific, where O₂ values are suboxic, it seems more likely that the increase in dissolved Fe is simply due to increased fluxes of Fe from the greater flux of sinking organic particulate material leaving the euphotic zone of this productive region.
4.4.2. *Westward Fe Increases in the Subtropical Gyre*

The distinct increase in surface and deep water Fe through Stations 7, 8, and 9 (Figure 3.21) in the subtropical gyre provides supporting evidence for increasing eolian inputs moving from the western N. Pacific to the central N. Pacific (see above). Bruland et al. (1994) suggested that the water column Fe inventory is controlled by 1) release from eolian dusts in the surface ocean 2) release of Fe from sinking particles in the water column balanced by 3) scavenging of iron onto refractory particles. It then seems somewhat logical that an increased flux of Fe to surface waters via the atmosphere would eventually result in an increased deep water Fe concentration.

Johnson et al. (1997) argue that the relative global constancy in concentration of dissolved Fe below 1000 m (∼0.6 nM) suggests that removal rates of iron decrease substantially at concentrations less than 0.6 nM. Organic complexation of Fe by ligands with a capacity to complex ∼0.6 nM Fe is a possible mechanism. A second possible mechanism is an equilibrium between the dissolved and particulate phases of Fe.

However, the 2002 IOC data set shows variable Fe concentrations below 1000 m ranging from ∼0.6 nM to >1 nM Fe. Boyle (1997) argues that a low atmospheric dust flux in the South Pacific is the likely cause of low Fe concentrations in the deep waters of the South Pacific. Perhaps, then, it follows that an enhanced dust flux would result in increased dissolved Fe fluxes to deep waters and that the organic ligands become saturated with respect to bound Fe. The result would then be an increase in dissolved Fe.
The increases in surface and deep water Fe in Figure 3.21 through St. 6, 7, 8, and 9 provide further support for the idea of increased fluxes of atmospheric dust fluxes in the central N. Pacific as opposed to the far western N. Pacific, contrary to the Duce model. This notion is also supported by the differences in Al profiles observed along the cruise track at these same stations. In regions of elevated atmospheric dust fluxes, scavenging-type Al profiles would be expected to be observed with higher concentrations in the surface and a decrease with depth. A shift occurs from somewhat conservative and nutrient type profiles at the subarctic gyre Stations 2 and 3 (Figure 2.16) to more scavenging type Al profiles in the subtropical gyre at Stations 7, 8, and 9 (Figure 2.21). Station 9 (ALOHA) shows a very distinct scavenging-type profile with surface water concentrations > 6 nM, indicative of significant mineral dust fluxes relative to stations further west towards Japan.

4.4.3. Subsurface Al Maximum

The subsurface Al maximum observed at Stations 1, 5, 6, and 7 likely originates from either outcrops along isopycnal transport of Al from a density surface that originates in an area of high atmospheric input or from an in-situ water column process such as the remobilization of vertically transported Al. Based on previous work suggesting that Al has very little redox chemistry and is removed from surface waters
with little biological recycling, (Moran and Moore, 1992), the notion that the maximum originates due to outcropping in a high dust area is most plausible.

The subsurface Al maximum is centered on potential densities ($\sigma_0$) of 25.25-25.60 and reaches 9 nM at St. 1 and ~ 6 nM at St. 5,6, and 7. Sea surface density from the Levitus (1982) March climatological dataset shows the surface outcropping of these potential densities in the N. Pacific between $32^\circ$N and $36^\circ$N in the far western N. Pacific off the coast of Japan and between $30^\circ$N and $45^\circ$N in the central and eastern N. Pacific. Thus, it is possible that the subsurface Al maximum originates in the surface waters near Japan due to coastal and/or atmospheric inputs and is advected through the mixed water region into waters of central N. Pacific. Secondly, it is possible that the Al maximum originates in waters of the eastern N. Pacific, where increased atmospheric dust fluxes are believed to be found, and then spreads westward.

At Station 5, where the Al subsurface maximum is very well-defined (Figure 3.18), the 25.25-25.60 $\sigma_0$ values cover the depth range from 100 m to 275 m. Over this range temperature and salinity range from 15.27°C to 17.1°C and 34.63 to 34.70, respectively. Levitus (1982) shows that these temperature and salinity ranges are found in both the far western subarctic Pacific between $32^\circ$N and $36^\circ$N and between $30^\circ$N and $45^\circ$N in the central and eastern N. Pacific. Thus, at this time it is not possible to discern between one area or another as a possible source of the subsurface Al maximum.
4.5. A Final Comment on Fe Solubility

A significant finding of previous work concerning Al and Fe concentrations in surface waters is the narrow range of Fe concentration values as compared to the much broader range of Al values. Measures and Vink (1999) report surface water Fe values in the southwest Atlantic of 0.4-1.4 nM (a 3.5-fold range) coupled with surface water Al values of 8-61 nM (a 7.5-fold range). These highest Al values were observed in regions of the Atlantic believed to receive significant inputs of Saharan dust. While somewhat different ranges of Al and Fe values was observed during the 2002 IOC cruise (0.1-1.2 nM Fe; 0.8-7 nM Al), the data can be used to examine the systematics of Fe and Al concentration in open-ocean surface waters and the role that Fe solubility plays.

The amount of Fe that can dissolve from atmospheric dust is probably limited by both the intrinsic solubility of the Fe in the mineral dust and the presence of organic ligands which facilitate Fe solubility control in the surface waters (Millero, 1998). Al and Fe data collected in various regions of the world's oceans can be used to obtain an estimate of the upper limit of Fe solubility (Figure 4.4).

If Fe were not under solubility control then it would be reasonable to expect that the surface water ratios of Al:Fe should roughly mirror those found in eolian material of continental origin (~ 4:1). However, inspection of Figure 4.4 clearly shows that Al:Fe ratios range from ~ 1 in waters of the Southern Ocean receiving very little atmospheric dust flux to ~ 90 in the western Atlantic under areas of significant dust inputs.
More importantly, it is found that a cap on Fe values appears at \( \sim 1.5 \text{ nM} \). In a few regions, e.g., the Central N. Pacific and the Arabian Sea, Fe values approaching 2 nM are observed. It is possible that Fe values > 1.5 nM are observed in surface waters during non-equilibrium periods such as soon after an atmospheric dust event. It should also be noted that the \( \sim 2 \text{ nM} \) Fe values in the Central N. Pacific data were observed just offshore of the Na Pali Coast of Kauai and are largely due to local landmass effects. Thus, it is possible that in open-ocean surface waters solubility control of Fe (III) and organic complexation limit the dissolved Fe concentration at \( \sim 1.5 \text{ nM} \). However, perhaps this number can increase during non-equilibrium periods of increased atmospheric input.
Chapter 5: Conclusions

As mentioned previously, the goals of this thesis were to estimate atmospheric dust fluxes to the western and central N. Pacific using surface water Al concentrations and compare these results with established model values. In addition, surface and upper water Fe concentrations in the subarctic N. Pacific would be examined to provide a relationship between dust deposition, Fe, and nitrate in terms of biological limitation. Finally, vertical Al and Fe profiles were used to examine the possible effects of atmospheric deposition in the water column.

Surface water Al values determined along the IOC cruise track indicate significant differences with the established Duce model of dust flux estimates to the surface waters of the northwest Pacific. While the Duce model predicts deposition values in excess of 10 g m\(^{-2}\) yr\(^{-1}\) in the far western N. Pacific near Asia, the maximum values observed based on surface water Al concentrations were 0.5 g m\(^{-2}\) yr\(^{-1}\) in the subtropical gyre. It is likely that the Duce model is over-estimating dust inputs to the region largely due to the high altitude of atmospheric transport of the Asian dust above the marine boundary layer.

Thus, not only do the 2002 IOC estimates show that the Duce model is perhaps over-predicting atmospheric input. They also show that the geographic variation in dust
flux is of greater inputs to waters of the central N. Pacific than the western N. Pacific, contrary to the established model of decreasing dust gradients from west to east.

These results indicate that ground-truthing of atmospheric dust models is clearly needed through increased sampling and remote platforms. Until the global fluxes of atmospheric dust can be estimated accurately, the idea of modeling the effect of varying dust deposition on global climate change seems somewhat premature.

Surface and upper waters of the western subarctic N. Pacific showed significant Fe limitation largely due to insufficient atmospheric dust fluxes. It was shown that the dissolved Fe concentrations in upwelled waters provided through deep winter mixing in conjunction with the minimal Fe provided via atmospheric input is insufficient to support complete drawdown of all of the surface mixed layer nitrate provided by the upwelling process in the region.

Thus, in regards to the previously-developed controversy of whether atmospheric dust inputs to the western subarctic N. Pacific are being over-estimated or whether a species other than Fe is causing biological limitations, the answer is now clear. Biological limitation in the western subarctic N. Pacific is occurring due to insufficient inputs of Fe to the surface waters via upwelling and atmospheric deposition.

Finally, Al and Fe vertical profiles along the 2002 IOC cruise track further support the previous findings regarding atmospheric inputs. Fe profiles show a clear increase in surface and deep water Fe moving from waters of the western subarctic region
into the central subtropical gyre towards Hawaii. In addition, scavenging-type Al profiles expected in areas of significant atmospheric input are only observed in waters of the central subtropical gyre. A significant Fe increase in the suboxic upper waters of the subarctic region and a distinct subsurface Al maximum were two interesting features also noted in the vertical sampling.
Figure 1.1 History of atmospheric CO$_2$ and dust through 4 glacial-interglacial cycles back to 420 kya as recorded in Vostok Ice Core, Antarctica (Petit et al., 1999).

Figure 1.2. Contemporary dust deposition estimates to the world's oceans in g / m$^2$ / yr with the calibration site location plotted in Figure 1.3 (Duce et al., 1991).
Figure 1.3. MADcow model calibration. Comparison of dust deposition estimates derived from surface water Al concentrations from locations shown in Figure 1.2 with independent dust estimates (see text for details).

Figure 1.4. 2002 IOC Cruise track. Vertical stations indicated in red. Dashed lines indicate Duce et al. (1991) dust deposition contours.
Figure 1.5. Summer (Jul.-Sep.) mean nitrate (μM) in the Pacific Ocean for year 2001. Courtesy of Ocean Climate Laboratory, NODC: World Ocean Atlas, 2001.
Figure 1.6. Spring (Apr.-Jun) mean nitrate (μM) in the Pacific Ocean for year 2001.
Figure 2.1 From Vink et al., 2000. Al and Fe FIA schematics connected to fish sampler. V1 and V2 are the 6-port inject/load valves. Flow rates of each reagent noted on peristaltic pumps are for a pump speed of 7.5RPM.

Fig. 2.2 Al fluorometer output (top) and Fe spectrophotometer output (bottom) for one fish sample and three standards run in duplicate. The mixed Al/Fe standards were prepared by adding the following: +0, +12.5, and +25 nM Al and +0, +0.63, +1.26 nM Fe. The underway fish sample corresponding to the first peak in both data outputs had the following concentrations: 7.42 nM Al and 1.07 nM Fe.
Figure 2.3. Al (top) and Fe (bottom) std. curves for the standard runs highlighted in Figure 2.2. Note: the Fe std curve peak heights are an average of the respective duplicate standard peak heights seen in Figure 2.2.
Figure 3.1. Surface water temperature (top) and salinity (bottom) for the 2002 IOC cruise as determined by R/V Melville underway sensor. Data shown is actual underway sensor data gridded and contoured using Generic Mapping Tools.
Figure 3.2. Surface water oxygen (μmol/kg) as determined from ship's underway sensors.
Figure 3.3. Nitrate (top) and phosphate (bottom) concentrations in the surface waters along the IOC 2002 cruise track. Concentrations are in μM.
Figure 3.4. Silicate concentrations (μM) in surface waters of the 2002 IOC cruise track.

Figure 3.5. Underway surface Al and Fe concentrations (nM) plotted against decimal day of the IOC 2002 cruise track. 3300 determinations were made in all.
Figure 3.6. Gridded Al (bottom) and Fe (top) surface water concentrations along the 2002 IOC cruise track. Concentrations are in nM.
Figure 3.7. SST and Salinity (top) and Al and Fe concentrations (bottom) for northeast transect between Stations 1 and 2. Decimal Day 8-11 corresponds to 35°N, 140°W through 42°N, 153° E heading towards Station 2.
Figure 3.8. Local Al maximum at decimal day 9.1 observed during general Al decrease during the transect between Station 1 and 2 from Figure 2.7.
Figure 3.9. Temperature and salinity (top) and Al and Fe (bottom) in the subarctic gyre. Decimal day 11-17 corresponds to the cruise leg within the subarctic gyre from 42.8°N, 153°W, northeast to 50°N, 167°E, and south to 44°N, 170.6°W. Station occupation is indicated by black arrows.
Figure 3.10. Temperature and salinity (top) and Al and Fe (bottom) for decimal day 16-22. This timeframe corresponds to the southward transit along 170.6°W longitude from 46.6°N south to 30.9°N. Station occupation indicated by black arrows.
Figure 3.11. Temperature and salinity (top) and Al and Fe (bottom) for decimal day 22-31. This timeframe corresponds to the eastward transit in the subtropical gyre between St. 7, 8, and 9 from 173.5°W longitude to 160°E longitude.
Figure 3.12. Potential temperature vs. salinity (T-S diagram) for Stations 1-9 and surface water transects between each Station.
Figure 3.13. Temperature, salinity, and oxygen contour plots for the upper 1500 m along the 2002 IOC cruise track. Station locations are given by black numbers located in the center of each plot frame. T, S, and O are in °C, ppt, and μmol/kg, respectively.
Figure 3.14. NO₃ (top) and SiO₂ (bottom) contour plots along the 2002 IOC cruise track. Station locations are given by black numbers located in each plot frame and tick marks indicate the depths sampled for nutrients at each respective Station.
Figure 3.15. Temperature, salinity, NO$_3^-$, and oxygen profiles for the upper 1500 m at the subarctic gyre Stations 2 (top) and 3 (bottom).
Figure 3.16. Total Dissolved Al and Fe profiles (0-1500 m) for Stations 2 (top) and 3 (bottom) located in the subarctic gyre.
Figure 3.17. Mixed water region Stations 1, 4, and 5 temperature and salinity profiles (left) and nitrate and oxygen profiles (right).
Figure 3.18. Total Dissolved Al and Fe profiles for the mixed water region Stations 1, 4, and 5. Note that Fe scale for Station 1 is different from that for Stations 4 and 5.
Figure 3.19. Temperature and salinity (left) and nitrate and oxygen (right) at the subtropical gyre Stations 6 (top) and Station 7 (bottom).
Figure 3.20. Temperature and salinity (left) and nitrate and oxygen (right) at the subtropical gyre Stations 8 (top) and Station 9 (bottom).
Figure 3.21. Total Dissolved Al and Fe profiles for the subtropical gyre Stations 6-9.
Figure 4.1. MADCOW model dust deposition estimates based on surface water Al concentrations. Values calculated using a mean partial Al solubility and varying mixed layer depth (see text for details).

Table 4.1. Mixed layer depth ranges for each transect of the 2002 IOC cruise. Mixed layer depths are in meters.

<table>
<thead>
<tr>
<th>Cruise Transect (Station#-Station#)</th>
<th>Mixed Layer Depth Range (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test-1</td>
<td>50</td>
</tr>
<tr>
<td>1-2</td>
<td>50-60</td>
</tr>
<tr>
<td>2-3</td>
<td>60-110</td>
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<td>3-4</td>
<td>110-26</td>
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<td>4-5</td>
<td>26-30</td>
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<td>6-7</td>
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<td>7-8</td>
<td>50-15</td>
</tr>
<tr>
<td>8-9</td>
<td>15-20</td>
</tr>
<tr>
<td>9-Oahu, HI</td>
<td>20</td>
</tr>
</tbody>
</table>
Figure 4.2. Surface water NO₃:Fe ratios along the 2002 IOC cruise track. Note that calculations were performed using a NO₃ concentration of 0.18 μM was used where nitrate concentrations were below detection limits.

Figure 4.3. Sea surface density from the Levitus (1982) March climatological dataset. Adapted from Qui (1995).
References


Smith, W. and Wessel, P. "Gridding with continuous curvature splines in tension." Geophysics, 55, 293-305.


