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DISSERTATION APPROVAL

The abstract and dissertation of Allan Hayes Vogel for the Doctor of Philosophy in Environmental Sciences and Resources - Biology were presented 2 December 1994, and accepted by the dissertation committee and the doctoral program.

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ABSTRACT

An abstract of the dissertation of Allan Hayes Vogel for the Doctor of Philosophy in Environmental Sciences and Resources - Biology presented 2 December 1994.

Title: Some relationships between sedimentary trace metal concentrations and freshwater phytoplankton and sedimentary diatom species composition

Sediments from 21 Oregon lakes were analyzed for seven metals (Fe, Mn, Zn, Cu, Co, Ni, V) in three forms (exchangeable, organic+sulfides, and oxyhydroxides+ oxides+ carbonates) using a sequential fractionation procedure. The summer epilimnetic filterable concentration of an eighth (Mo) was also determined. Sedimentary diatom remains and summer phytoplankton populations of the lakes were correlated with the 22 metal parameters and with conservative water chemistry parameters, estimators of lake productivity, and watershed geology.

Both the sedimentary metals and the two populations of primary producers correlated best with the ecoregions of Omernik and Gallant (1986).

A number of species possessed correlations with specific trace metal extractions or ratios of those extractions. Bloom-forming *Anabaenas* strongly correlated with sedimentary organic and filterable epilimnetic nickel. Possible Ni limitation of this group was observed in one Cascade lake (Lava). The ratio of organic nickel to cobalt appeared to control the abundance of several sedimentary diatoms. Organic vanadium strongly correlated with a number of diatoms, particularly in the genera, *Cyclotella* and *Fragilaria*. Possible V pollution was observed in one lake (Woahink), and frustule remains of *C.*

stelligera significantly increased with increasing total sedimentary V concentrations there. Zinc was the trace metal most frequently found to apparently limit diatom growth. Diatoms may have developed three different responses to Zn limitation; the three groups have been labelled affinity-, velocity-, and (possibly) storage- specialists following Sommer (1985). Possible Zn pollution was observed in two lakes (Oswego and Clear).

Phytoplankton and sedimentary diatoms weakly correlated with sedimentary iron by comparison to Ni, V, or Zn. Few strong relationships were observed with manganese, copper, or cobalt. No statistically significant correlations were found with molybdenum, and few correlations between a conservative chemical parameter and a species of phytoplankton were found.

There was poor correlation between trace metal concentrations and lake productivity, despite frequently observed correlations between individual species and particular trace metal fractions.

These findings suggest that variations in absolute trace metal concentrations, and/or ratios, may be important factors for controlling species distribution, but have relatively little influence upon lake primary productivity or standing stocks.

SOME RELATIONSHIPS BETWEEN SEDIMENTARY TRACE METAL
CONCENTRATIONS AND FRESHWATER PHYTOPLANKTON AND
SEDIMENTARY DIATOM SPECIES COMPOSITION

by

Allan Hayes Vogel

A dissertation submitted in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

ENVIRONMENTAL SCIENCES AND RESOURCES - BIOLOGY

Portland State University

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I. Introduction

A. Purpose of Study

1. Objectives

This study investigated the role of eight trace metals in controlling the distribution of individual species of phytoplankton, including cyanophytes, and of epibenthic diatoms. Previous research has indicated that primary productivity appears to be controlled by light, by three major limiting nutrients, phosphorus, nitrogen and silicon, and by predation (Allen and Koonce 1973; Reynolds 1984; Sommer 1984; Tilman 1982). Furthermore, these ecological factors have been shown to influence which of the major taxonomic groups of phytoplankton is dominant. For the most part however, it has not yet been possible to explain which individual species within the major taxonomic groups are likely to be present. Trace metals have, however, been implicated in determining the species composition of some natural waters (Frey and Small 1980). This research seeks to verify these observations for freshwater phytoplankton assemblages.

In this study, the specific objective was to describe the distribution of seven trace metals in three different chemical forms from the sediments of 21 Oregon lakes as well as the summer epilimnetic dissolved concentrations of an eighth metal from the water column of these lakes, then to compare the patterns found with the species distributions of phytoplankton and epibenthic diatoms in these lakes. The comparisons from lake to lake between phytoplankton, diatom remains in the sediments, and sedimentary trace metals in their exchangeable, organic, and total available fractions were designed to test the hypothesis that metals, or metal ratios, can determine species composition in freshwater ecosystems. The trace metals chosen for analysis include six of the universally physiologically-essential metals for algae (iron, manganese, zinc, copper, cobalt and vanadium) and a metal (nickel) of known toxicity but which may also be essential for some species. The role of another essential metal (molybdenum) was estimated from its summer epilimnetic dissolved concentrations in these lakes.

The general scientific goals of this research are to indicate whether or not the primary hypothesis is valid for freshwater ecosystems and to suggest which trace metals, or metal ratios, are important with respect to species composition in unpolluted ecosystems.

2. Rationale for Specific Approach

a. A Comparative Field Study of Oregon Lakes

While Frey and Small (1980) experimentally demonstrated that the primary hypothesis of this research is valid, their study failed to verify it in freshwater ecosystems for several reasons. First, the system that they analyzed was estuarine, not freshwater. As a consequence, the species assemblage studied is not present in freshwater, and as Frey and Small indicated, salinity effects upon species composition frequently overwhelm other considerations. Second, the range of water chemistry is much more variable in freshwater than in marine or estuarine waters which typically change only in total salt concentration (the proportion of sodium to magnesium, for example, does not significantly vary between 0.5 and 35 parts per thousand of salinity - Sverdrup, et al. 1942) or in the concentration of nutrients. Large changes in the ratios between different cations (including metals) are frequently observed in freshwaters however (Hutchinson 1957; Wetzel 1975). Thus, if a large and highly diverse set of lakes is sampled for both metals and plankton, the results should provide indirect evidence to test the hypothesis.

The physical setting of Oregon represents a unique opportunity not available elsewhere to test this hypothesis. Such research could not be attempted, for example, in the Midwest, northeastern North America or Western Europe due to the relative uniformity of climate and superficial geology of those areas outside of montane regions. The success of this research has been considerably enhanced by the diversity of Oregon's climate, geology and lake types. A comparison of lake types of Oregon (Johnson, et al. 1985), to the findings of Sparling and Nalewajko (1970) in Ontario, to those of Rippey and Gibson (1984) from Northern Ireland, or to the descriptions of England's Lake District (Macan 1970) clearly demonstrates the validity of this assessment (Seven groups in Oregon vs. four in Ontario, two in Northern Ireland, and five in the English Lake District). Furthermore, Johnson, et al.'s classification based upon lake origin may be a conservative estimate of the different types of lakes possible in Oregon if Omernik and Gallant's (1986) ecoregion classification of the Pacific Northwest is correct (See Figure 2, p. 64). Whittier, et al (1988) found distinct differences in the aquatic biota of lotic communities in Omernik and Gallant's eight major ecoregions. In addition, Omernik and Gallant's classification

system ignored a geologically and chemically important subdivision of lakes in the Coastal ecoregion, the lakes in and immediately behind the sand dunes such as Woahink, Eel, Siltcoos, Tahkenitch, Clear, Mercer, and Munsel around Florence and Reedsport on the central coast, or Cullaby on the north coast.

A second major advantage that Oregon offers is that there is no significant acid precipitation in this state yet, though the geology of Western U.S. mountain regions makes them very sensitive to this type of pollution (El-Ashry, et al. 1985; Tonnessen 1984). Recently low levels of acid precipitation, mainly in the form of snowfall, have been found in the Washington Cascades, in the Californian Sierra Nevada (Laird, et al. 1986), and in the Colorado Rockies (Baron, et al. 1986). Laird, et al. attributed the acid precipitation in the Washington Cascades and Sierra Nevada to automobile exhaust and coal combustion in the Puget Sound region, and in the San Francisco and Los Angeles-San Diego regions, while Baron, et al. believed the low pHs in the Rockies came from pollution originating in the Los Angeles-San Diego and Phoenix-Tucson regions. The lack of acid precipitation is an important local characteristic for field work on trace metals since acidification causes major alterations of aqueous and sedimentary metal chemistry (Brække 1976; Carignan and Nriagu 1985; Cowling 1982; Davis, et al. 1983; Drabløs and Tollan 1980; Henriksen and Wright 1978) as well as large changes in the biota of affected lakes (Drabløs and Tollan 1980; Schindler 1985; Schindler, et al. 1985).

b. Sediment Analysis instead of Water

Chemical analysis of lake sediments was selected as the primary focus of this research because single water samples do not provide an adequate characterization of the aqueous chemistry of a lake. Lake sediments have been found to give better estimates of mean ecosystem conditions than infrequently collected water samples (Førstner and Wittman 1979; Håkanson and Jansson 1983). This is due to a number of factors. First, the waters of lakes are in a dynamic equilibrium for some chemical reactions, not in equilibrium for others, and in a steady state for still others (Morgan and Stone 1985). This phenomenon is caused by the varying time scales of the different possible chemical reactions. Second, seasonal changes occur in trace metal concentrations in the euphotic zone due to both biological and chemical processes (Sholkovitz and

Copland 1982; Wrench and Measures 1982), and third, the dissolved trace metal concentrations in the epilimnion are frequently undersaturated to a varying degree due to adsorption onto precipitating iron hydroxides (Tessier, et al. 1985) or to assimilation by the phytoplankton. As a consequence, using a single water sample to estimate the average trace metal concentrations in the surface waters of a lake cannot be an accurate measurement of the equilibrium conditions present in that lake. "(A)nalysis of a sediment sample always means integration over a certain time period, the length of which depends on the thickness of the sediment layer. Thus, sediment analyses represent a longer time period than a single situation analysis of a water sample, and ... reliable results (as to the mean background and environmental trends) can sometimes be obtained by one sediment survey (Håkanson and Jansson 1983, p.95)." This time integrative function can be quite useful in determining the actual trace metal requirements of algal species.

Another contribution of lake sediment studies is determining the activity of biological components in biogeochemical cycles. The partitioning of some metals into the particulate phase and their subsequent transport to the sediments is controlled in the open ocean by the affinity of phytoplankton for these elements (Lyle and Collier 1987; Morel and Hudson 1985); this mechanism may exist in freshwater as well.

Finally, vertical profiles of potential heavy metal pollutants in lake sediments have been shown to represent accurately the environmental history of the watersheds of these lakes and, in some areas, their regional airsheds as well (Charles and Norton 1986; Crecelius 1975; Davis, et al. 1983; Davison, et al. 1985; Nriagu 1983; Nriagu and Wong 1983).

B. Literature Review

1. Physiological Roles of Trace Metals

While studies of the mineral nutrition of plants or of laboratory populations of algae and cyanophytes began as early as the 1930s (Bowen 1966) or before (e.g., Liebig), investigations into the trace metal composition and requirements of natural populations of phytoplankton did not begin until the 1950s (Nicholls, et al. 1959; Vinogradova and Kovalskiy 1962). The earliest studies were frequently compromised by contaminants however (Collier and Edmond 1981;

Martin and Knauer 1973). As Collier and Edmond pointed out “(e)xperience gained in the collection of water samples for dissolved trace elements suggests that it is very likely that many of the reported plankton analyses are seriously contaminated. This fact, combined with other sampling and analytical problems ... , gives one very little confidence in using currently (as of 1981) reported plankton data in trace element geochemical models. Notable exceptions include analyses by Martin and Knauer (1973) who made serious attempts to address the problems of contamination in their samples (p.791).” Martin and Knauer (Knauer and Martin 1972, Martin and Knauer 1973) found median dry weight concentrations in rapidly growing marine phytoplankton of 224 ppm Fe, 6.1 ppm Mn, 19 ppm Zn, 3.2 ppm Cu, 1.9 ppm Ni, and concentrations below 3.1 ppm V, 2.0 ppm Mo, and 1.0 ppm Co. These median values demonstrated great spatial variability as well as variability due to physiological condition of the population being sampled (Similar findings were made by Vogel (1973) who followed identical or equivalent anti-contamination techniques to Collier and to Martin and Knauer independent of these authors).

The eight trace metals studied herein are required by cyanophytes, eukaryotic algae and higher plants in varying amounts. For higher plants, the molar ratios relative to phosphorus are approximately $3 \cdot 10^{-2}$ Fe, $2 \cdot 10^{-2}$ Mn, $5 \cdot 10^{-3}$ Zn, $2 \cdot 10^{-3}$ Cu, and $2 \cdot 10^{-5}$ Mo (Salisbury and Ross 1969). Requirements for Co and V in higher plants were not described by them, nor was Ni known to be a required inorganic nutrient at the time that they wrote their text. Morel and Hudson (1985) calculated molar ratios relative to P of $0.5\text{--}1.5 \cdot 10^{-2}$ Fe, $0.5\text{--}1.5 \cdot 10^{-2}$ Mn, $3 \cdot 10^{-3}$ Zn, $1.5 \cdot 10^{-3}$ Cu, and $3 \cdot 10^{-3}$ Ni for plankton.

Four of the eight metals investigated during this research (iron, molybdenum, nickel, and vanadium) have been found to be required for the nitrogen metabolism of algae and cyanophytes, either in fixation, uptake of aqueous forms, or in intracellular transformation. Only the non-ferric metals involved with electron transport in both respiration and photosynthesis (manganese and copper), zinc, a trace metal found in a wide variety of regulatory roles, and cobalt are more abundant in plants than are the non-ferric metals involved in nitrogen metabolism (Raven, et al. 1986). Since a number of researchers (e.g., Raven 1988, Vitousek and Howarth 1991) believe that nitrogen limitation is the main restriction on net primary productivity both on land and in the ocean

as well as in some lakes, a considerable amount of work involving trace metals have focused on aquatic systems where nitrogen is limiting. The second largest area of aquatic trace metal research has been toxicity studies, mainly of copper, zinc, and nickel. Iron limitation studies make up most of the rest of the investigations into the physiology of trace metals in aqueous environments.

Iron is known to be essential for algae and cyanophytes in four important physiological processes: photosynthesis, respiration, chlorophyll synthesis, and nitrogen assimilation (Table 1, Huntsman and Sunda 1980, Raven 1988). The first three roles were demonstrated for algae as early as the 1950's or earlier (Wiessner 1962). Manganese is required as the activating enzyme for splitting water in photosystem II of all photosynthetic organisms (Table 1, Sunda 1988, Sandmann and Böger 1983, Huntsman and Sunda 1980, Salisbury and Ross 1969). Zinc has been found to be an essential enzymatic activator in a wide assortment of cellular compounds (Table 1). Most cellular copper is found in plastocyanin which is part of the photosynthetic electron transport system (Table 1). Cobalt is primarily present in algae as vitamin B₁₂ (Sunda 1988). Nickel is another metal involved with nitrogen transformation and metabolism (Table 1). Spencer (1980, Spencer and Greene 1981) has demonstrated that cyanophytes have a higher tolerance (and apparently a higher requirement) for this trace metal than do either greens or diatoms. Its involvement in nitrogen fixation (Table 1) is apparently the cause for Spencer's findings as excess nickel has been demonstrated to be quite toxic (Wood and Wang 1983). The physiological role of vanadium in cyanophytes, eukaryotic algae, and higher plants is not well understood (Bollard 1983), but it appears to be involved in the synthesis of chlorophyll and other porphyrins by green algae (Table 1). Molybdenum is associated with nitrogen metabolism in both cyanophytes (Rueter and Petersen 1987) and eukaryotic algae (Fogg 1962). The major metabolic role of molybdenum is as a co-factor for nitrogenase (Fogg, et al. 1973).

An additional important physiological aspect of V is its narrow optimal range. Patrick (1978, et al. 1975) has shown that V concentrations over 100 ppb ($\sim 2 \mu\text{g}\cdot\text{l}^{-1}$) significantly reduce photosynthesis by freshwater algae. Diatoms are more sensitive to V than either cyanophytes or greens (Lee 1983).

Relatively little is actually known about the physiological essentiality of trace metals despite all of the investigations done so far. Nor is much known

Table 1: Known Physiological Functions of Trace Metals

Function	Reference(s)
<u>a. Iron</u>	
electron transport in photosynthesis and respiration	24, 34
nitrogen assimilation and transformation	6, 21, 23, 26, 28, 29, 35, 36, 37
nitrogenase	34
nitrate and nitrite reductase	34
ammonium assimilation by glutamine and glutamate synthetases	23
catalase, peroxidase, some eukaryotic and all cyanophytic superoxide dismutases	9, 14, 23, 32, 34
<u>b. Manganese</u>	
water splitting in photosystem II (produces gaseous oxygen)	11, 30, 32, 34
cyanophytic superoxide dismutases	32, 34
activating co-factor for pyruvate carboxylase and isocitric decarboxylase	10, 12, 14
a ribozyme	3
<u>c. Zinc</u>	
essential enzymatic activator for alkaline phosphatase, carbonic anhydrase, DNA and RNA polymerases, phosphate esters hydrolysis	34
eukaryotic superoxide dismutases	9
alcohol dehydrogenase	32
NADH, lactic acid, and glutamic acid dehydrogenases	30
carboxypeptidase	30
silicate metabolism	27
some ribozymes	22
some gene transcription enzymes	17
<u>d. Copper</u>	
plastocyanin	30
eukaryotic superoxide dismutases	9
cytochrome c oxidase	32, 34
ascorbate, galactose, and benzylamine oxidases	32
tyrosinase	32
<u>e. Cobalt</u>	
vitamin B12	34
required by all nitrogen-fixers	1, 8
some other cyanophytes	8
some diatoms	5, 20
green algae	4
chrysophytes	31

Table 1: Known Physiological Functions of Trace Metals (cont.)

f. Nickel

urease	18, 34
hydrogenase	33
required in nitrogen-fixation	2, 19

g. Vanadium

porphyrin (and apparently chlorophyll) synthesis	1, 13, 15, 16
alternative nitrogenase activator	25

h. Molybdenum

nitrogenase	8, 28
co-factor in nitrate reductase	7

Key: 1) Bollard 1983, 2) Dalton and Evans 1986, 3) Dange, et al. 1990, 4) Droop 1962, 5) Droop 1973, 6) Evans and Russell 1971, 7) Fogg 1962, 8) Fogg, et al. 1973, 9) Fraústo da Silva and Williams 1991, 10) Goodwin and Mercer 1972, 11) Huntsman and Sunda 1980, 12) Kendrick, et al. 1992, 13) Lee 1983, 14) Lehninger 1982, 15) Meisch and Bellman 1980, 16) Meisch, et al. 1977, 17) O'Halloran 1993, 18) Oliveira and Antia 1984, 1986, 19) Papen, et al. 1986, 20) Patrick 1977, 21) Postgate 1987, 22) Pyle 1993, 23) Raven 1988, 24) Raven, et al. 1986, 25) Robson, et al. 1986, 26) Rueter and Ades 1987, 27) Rueter and Morel 1981, 28) Rueter and Petersen 1987, 29) Rueter, et al. 1990, 30) Salisbury and Ross 1969, 31) Sandgren 1988, 32) Sandmann and Böger 1983, 33) Smith 1983, 34) Sunda 1988, 35) Vitousek and Howarth 1991, 36) Wurtsbaugh 1988, 37) Wurtsbaugh and Horne 1985

about their subcellular distribution, intracellular transport mechanisms, and storage sites (O'Halloran 1993). Iron has probably been studied in the most detail of any of these metals, but less than 30 percent of the requirement for this element as a catalyst for physiological processes in plants has been identified (Hewitt 1983). The physiological role of iron in algae is even less completely known. One study (Harrison and Morel 1986) could explain no more than 16% of the cellular iron required by a marine diatom, *Thalassiosira weissflogii*. Another study (Hutchins, et al. 1988) calculated that the cellular iron inventory only accounts for some 10 to 16% of the amount required. Luxury uptake, structural requirements, and inefficient utilization of some metallo-enzymes may explain part of the discrepancy, but iron and several other trace metals have been demonstrated to limit algal growth at cellular concentrations far above the known requirement per cell of these metals as catalysts (Raven 1988). Furthermore, important new cellular compounds containing trace met-

als are being discovered at an ever increasing rate (e.g., Mn and Zn-containing ribozymes, Pyle 1993) as well as important new physiological roles for trace metals (e.g. Zn fingers in gene expression and Cu and Fe-containing sensors, O'Halloran 1993), so it is likely that there still are a number of physiological functions of trace metals yet to be found, as well as learning the intracellular distribution of these elements. Consequently, this section will probably be outdated quickly, especially given the fact that several of the now widely-recognized functions of these trace metals were unknown when this research began.

2. Evidence Supporting Limitation of Algae and Cyanophytes by Trace Metals

Three characteristics should be apparent when a trace metal, or metals, is (or are) limiting growth of either cyanophytes and/or eukaryotic algae (Rueter and Petersen 1987). These are 1) a positive correlation between availability of the metal in the water and the amount of metal in the organism, 2) a deficiency of the metal should cause a reduction of specific metal dependent processes which can be reversed with the addition of the particular metal, and 3) there should be a specific cellular mechanism for uptake of the trace metal at limiting concentrations. Unfortunately the third characteristic has been largely ignored in the ecological literature, and there exists a considerable confusion between total concentrations and the actual available metal concentrations. For some metals, such as copper, this distinction is not important, but for others, such as iron, a significant majority of the metal present in the water column is apparently unavailable for algal and cyanophytic uptake. Given the difficulties inherent in measuring actual availability, even with chemically ultra- clean techniques, most of the direct evidence for trace metal limitation has centered around demonstrations of the second characteristic through the use of variously configured nutrient addition experiments.

A fourth characteristic, though indirect evidence, has been frequently cited in the literature (e.g., Sholkovitz and Copland 1982). This highly useful approach is to examine either the seasonal (e.g., Wrench and Measures 1982) or vertical (e.g., Collier 1984) distribution of the dissolved forms of the metal of interest and to compare the observed distribution with that of a major nutrient which is known to be limiting phytoplankton in the area studied. However, a major restriction upon this secondary criterion is that all possible geochemical

explanations need to be ruled out before unreservedly attributing any observed variations to the effects of biological uptake. Conversely, the lack of seasonal or vertical differences does not prove the lack of biological uptake because, first, a negative can not be proven but, more importantly, such a result may only demonstrate that local geochemical regeneration rates are exceeding biological demands, thus the metal is not limiting in that particular environment. Species-specific responses to the major cations are examples of the latter situation.

a. Iron

Although difficult to measure accurately, dissolved iron concentrations have long been hypothesized to limit phytoplankton growth and nitrogen fixation in both the ocean and some freshwater environments (Menzel and Ryther 1961; Rodhe 1948; Schelske 1962, Schelske, et al. 1962). Glooschenko and Curl (1971) first demonstrated apparent primary production enhancement due to iron off the Oregon coast and in the mid-Pacific in the late 1960s. About the same time Lewin and Chen (1971) found that most of the iron present in seawater was not available for diatom uptake, and Sakamoto (1971) demonstrated that the availability of iron rather than its total concentration was the important factor for iron limitation in freshwater. Goldman (1972) found that iron additions increased phytoplankton growth in three Sierra Nevadan lakes including Lake Tahoe, and iron has been shown to be the most important limiting nutrient in a saline, meromictic lake in Nevada (Priscu, et al. 1982). Iron limitation of marine phytoplankton has been suggested as a possible evolutionary force selecting for new species formation (Brand, et al. 1983, DiTullio, et al. 1993); this phenomenon could also exist among freshwater species.

The failure of marine phytoplankton to exhaust phosphorus and nitrogen in the Southern Ocean and subarctic and equatorial Pacific, known as the High Nutrient, Low Chlorophyll (HNLC) paradox, has intrigued biological oceanographers for years (Chisholm and Morel 1991). The prevailing hypothesis has long been that zooplankton grazing kept primary productivity down, though light and temperature limitations in the Southern Ocean were also thought to play a role. However, using improved techniques, Martin and Fitzwater (1988) confirmed the iron deficiency in the North Pacific originally found by Glooschenko

and Curl (1971). They hypothesized (Martin, et al. 1990) that iron additions from terrestrial dust fluxes might control atmospheric CO₂ concentrations, which lead to the “Geritol solution for Global Warming.” This hypothesis was publicized by the national mass media. This press coverage stirred up great concern among oceanographers and resulted in a special ASLO symposium on the subject in February 1991 (Chisholm and Morel 1991). The consensus statement from this symposium was that the hypothesis of iron limitation in HNLC areas deserved serious attention, but that use of iron to enhance phytoplankton growth and so to solve global warming was probably an inadequate remedy (Chisholm and Morel 1991).

Whether or not iron could limit oceanic phytoplankton was approached in different ways. Morel, et al. (1991) looked at all of the potentially limiting trace metals in seawater and concluded, on the basis of diffusion rates and ambient concentrations of these metals, that both iron and zinc could limit growth, but not manganese nor nickel. Coale (1991) found in a bioassay series that iron additions increased growth rates and standing crop estimates (chlorophyll *a* and cell densities), manganese mainly increased just diatom biomass, and zinc, due to naturally-occurring ligands (Bruland 1989) making it quickly unavailable, had the least beneficial effect of the trace metals studied.

Chavez, et al. (1991) observed that phytoplankton limitation in the equatorial Pacific is due to a combination of factors including grazing, iron limitation, and sinking, and that iron additions had a differential effect upon the different size fractions of equatorial oceanic phytoplankton. Work by both Frost (1991) and Miller, et al. (1991) in the subarctic Pacific supported the combination effects hypothesis. Buma, et al. (1991) also found that there was a species shift towards diatoms in iron addition experiments done in the Weddell and Scotia Seas, but that other factors appeared to be the primary controls upon phytoplankton growth there. The species-specific nature of iron additions was also apparent in experiments by Banse (1991). However, light limitation remained a valid alternative to iron limitation or grazing pressure in the Southern Ocean (Nelson and Smith 1991, Mitchell, et al. 1991). Nor has a low rate of nitrate uptake there been adequately demonstrated (Cochlan, et al. 1991).

Sunda, et al. (1991), however, questioned whether iron enrichment would work at all, on the basis of their findings of low iron requirements for oceanic

phytoplankton species. Brand (1991) found a similar phenomenon. Hutchins, et al. (1993), nonetheless, demonstrated that iron recycling between different species of marine plankton, though less efficient than nitrogen recycling, was apparently a major factor in maintaining primary productivity in HNLC areas, again stressing the center role of iron nutrition in the pelagic habitat.

A field test of the iron hypothesis was performed in the fall of 1993 (Kerr 1994). In this experiment a solution of iron sulfate was directly added to an eight by eight kilometer region of the equatorial Pacific and the resulting phytoplankton growth monitored. The iron concentration was increased over the ambient concentration by 100 fold by this addition. According to Richard Barber of IronEx, "the results were spectacular (Kerr 1994, p.1089)." The added iron caused a doubling of the phytoplankton within the first three days; however after that time, its effect ceased, apparently due to the added iron precipitating out of the euphotic zone. The same process of iron precipitation out of the euphotic zone also appears to naturally occur downstream from the Galápagos according to scientists who participated in IronEx (Kerr 1994).

Colimitation of freshwater phytoplankton by iron and nitrogen, a consequence of the role of iron in nitrogen metabolism, is particularly important in some cold, deep, oligotrophic lakes as the iron which enters such lakes has little chance of being assimilated by nitrogen fixers, and thus the lake can never accumulate enough nitrogen to become phosphorus limited (Rueter and Petersen 1987). Several Cascade lakes, specifically Crater and Blue (Santiam Pass), are good examples of this phenomenon (Rueter and Petersen 1987).

A second important phytoplankton growth factor which iron concentrations interact with is light. Increased amounts of iron have been shown to improve photosynthetic rates at low light intensities (Rueter and Ades 1987).

Specific uptake sites and mechanisms (Rueter and Petersen's third criterion) have been demonstrated for iron by diatoms (Anderson and Morel 1982, Harrison and Morel 1986, Hudson and Morel 1990). Harrison and Morel (1986) found that the neritic marine diatom *Thalassiosira weissflogii* does not regulate its iron uptake by the free ferric iron concentration in the medium. Instead, iron uptake by this diatom appeared to be controlled by some sort of negative feedback from within the cell. "Iron uptake... follows classic Michaelis-Menton kinetics, supporting a simple porter-binding model for iron transport (Harrison

and Morel 1986, p. 996).” Variability for iron in $r_{\max}$, the maximum rate of nutrient uptake per cell, is apparently due to variation in the number of porter sites for this element, not increases in turnover rate nor changes in photosynthetic and respiratory rates. Apparently diatoms have developed a similar type of homeostatic mechanism to regulate intracellular trace metal concentrations that they have for major nutrients such as nitrogen, phosphorus, and silica (Harrison and Morel 1986). Hudson and Morel (1990), through a series of ^{59}Fe pulse-chase experiments, observed a direct iron uptake rate of 10^{-17} mol Fe cell^{-1} with observed turnover times of 6-20 minutes for the coastal coccolithophore *Pleurochrysis carterae* and the neritic diatom *Thalassiosira weissflogii*. These rates and the observed half-saturation constants of iron uptake, 0.7 nM and 3.1 nM, for *P. carterae* and *T. weissflogii*, respectively, fit a standard transport model by specific, surface-associated sites. However, they noted that the number of transport sites for the diatom is rather large when compared to the cell Fe quota (5-25%), suggesting that the transport molecule is rather small, and supporting the observation that the uptake rate of iron through the cell membrane is relatively slow. Nevertheless both species are able to transport iron across the cell membrane at 14% for *P. carterae* and 20% for *T. weissflogii* of the maximum aqueous diffusion rate for this metal. Since the cellular limit for diffusion flux rates is about two-thirds of the maximum rate (Hudson and Morel 1990), this means that both inshore species are approaching the theoretical physical capability for iron uptake. Since this is a universal physical limitation of the iron uptake system, the only way for phytoplankton to adapt to the very low iron concentrations of the open ocean, or of ultraoligotrophic lakes, is to either become smaller or to reduce their cellular iron quota. Although cells apparently do both, there appears to be a limit to the minimum cellular iron requirement (Brand, et al. 1983), suggesting that cells under severe environmental iron deficiency should be smaller than phytoplankters growing under richer conditions (Hudson and Morel 1990). This phenomenon could thus explain the increases in numbers of diatoms observed by Martin, et al. (Martin and Fitzwater 1988, Martin, et al. 1989) when iron is added to iron-deficient oceanic water, and “since growth on NO_3^- increases the cellular requirements for Fe above that required for growth on organic N or NH_3 (Rueter and Ades 1987; Raven 1988), larger phytoplankton may simulta-

neously require more Fe and have more difficulty obtaining it in sufficient quantities. Thus, Fe may only limit growth rates of large organisms, yet still exert a significant influence on NO_3^- utilization and new production in the open ocean (Hudson and Morel 1990, p.1019)."

Iron deficiency is apparently particularly important for cyanophytes. Morton and Lee (1974) found that iron enrichment enhanced the growth of both nitrogen fixing and non-nitrogen fixing freshwater cyanophytes over green algae in mixed laboratory cultures while Lange (1974) showed that there was species competition by cyanophytes for this element when it was limiting as well as species-specific uptake rates. Dissolved iron (as determined by filtration through a $0.45\ \mu\text{m}$ pore filter) was found to specifically enhance cyanophyte growth in a freshwater lake by Elder and Horne (1977) and to increase the rate of heterocyst formation by nitrogen fixers. Nitrogen fixing cyanophytes may require up to ten times as much iron as when grown on nitrate (Lammers 1982), and iron limitation can specifically restrict nitrogen fixation in eutrophic lakes (Wurtsbaugh and Horne 1983). Given this information, Rueter (1982) was the first to hypothesize that the lack of iron in the world ocean might be responsible for the scarcity of autotrophic marine nitrogen fixers. Subsequent work by Rueter and others (Carpenter, et al. 1987, Rueter 1988, Rueter, et al. 1990) indicate that the cyanophyte *Trichodesmium* accounts for almost all of the pelagic nitrogen fixation in the world ocean, or up to a fourth of the total marine nitrogen fixation, and that natural populations of this cyanophyte frequently appear to be iron limited, so thus may limit primary and secondary productivity in the tropical portions of the world ocean.

One mechanism by which cyanophytes enhance the available iron concentration in freshwaters for their use has been through the production of siderophores (Armstrong and van Baalen 1979). These extracellular compounds bind with iron and enable the secreting cyanophyte to utilize the bound trace metal, thus conferring an advantage to the secretor over eukaryotic algae (Murphy, et al. 1976, Paerl 1988). Siderophores also reduce the free ion activity of copper, hence its toxicity to cyanophytes (McKnight and Morel 1979, 1980, Paerl 1988). Consequently, siderophore-secreting cyanophytes gain two competitive advantages over other species, and under conditions of water bloom formation and stable mixing conditions, siderophore production probably enhances cyano-

phyte growth (Rueter and Petersen 1987). The only species of eukaryotic algae which seems to have developed this mechanism for assimilating iron is a marine dinoflagellate, *Prorocentrum minimum* (Trick, et al. 1983); however, its production rate of siderophores is lower than that of the cyanophytes.

A second group of freshwater primary producers which require high iron concentrations are the chrysophyte microflagellates (Sandgren 1988). These eukaryotic organisms are abundant in the picoplankton of oligotrophic lakes and possess a very low absolute need for phosphorus with the consequence that they become less abundant with increasing eutrophication (Sandgren 1988). Sandgren believes that the great abundance of chrysophytes in humic lakes combined with their near absence in hard water, high alkalinity lakes suggests "that chrysophytes may be inferior to some other algae (cyanobacteria, diatoms, green algae) in sequestering iron in clearwater lakes. There is clearly a need for a well-constructed experimental study of chrysophyte seasonality and growth that incorporates measurement and manipulation of chelation capacity, iron concentration, and molecular forms of iron (p.61)."

While natural occurring concentrations of iron almost exclusively limits phytoplankton by being present in lower than optimal concentrations, Rueter and Ades (1987) were able to push iron concentrations in media up to the verge of being toxic (10^{-6} M Fe). They also noticed deleterious effects from too much iron in field studies. Nevertheless, this is probably a highly unusual event, short of a few, very localized, situations.

b. Manganese

Manganese is an essential trace metal which may be limiting in natural waters. Manganese, acting synergistically with phosphate, was first found to limit freshwater phytoplankton growth in Lake Superior by Shapiro and Glass (1975). Unfortunately, little work on the nutritional requirements of freshwater eukaryotic phytoplankton for this metal has been done since their study. Manganese is also known to limit marine phytoplankton however (Huntsman and Sunda 1980, Brand, et al. 1983, Sunda 1988), with a potential for species selectivity due to different requirements for this metal (Brand, et al. 1983, Sunda and Huntsman 1986). Cellular uptake of manganese follows the saturation kinetics model for carrier mediated transport across the outer cell

membrane, cellular manganese concentrations are regulated by a negative feedback system, and uptake is proportional to the free manganese ion concentration (Sunda and Huntsman 1986). Both tested diatoms appear to have rather narrow manganese optima which overlap the free ion concentration in the environments from where they were originally collected (the low manganese environment of the Sargasso Sea for *Thalassiosira oceanica*, and a high manganese-containing estuary for *T. pseudonana*), providing evidence supporting the importance of ambient free manganese concentrations in influencing phytoplankton evolution (Sunda and Huntsman 1986).

Manganese can apparently be toxic for many species of freshwater cyanophytes (Patrick, et. al. 1969), as was first demonstrated by Gerloff and Skoog (1957). At least one species of *Oscillatoria*, *O. rubescens*, is resistant to manganese toxicity however (Fuhs 1974). Although calcium concentrations play a role in controlling this toxicity (Gerloff and Skoog 1957, Patrick, et al. 1969), little else is known about the extent to which manganese may limit cyanophytes in nature. (*Anabaena flos-aquae* and *Microcystis aeruginosa* have been grown in defined AAP medium (U.S. EPA 1971) at two Mn levels (Vogel 1976 unpublished data). Small, species-specific, lags to the exponential growth phase were observed at the higher level. These results suggested a mechanism to explain Patrick, et al.'s finding that diatoms outcompete cyanophytes at these levels of Mn, but confirmation of these results was not performed.)

c. Zinc

Zinc can be present as both a limiting nutrient through deficiency and by occurring in toxic quantities (Sunda 1988). Biological utilization of this metal appears to be a function of the free ion concentration (Bates, et al. 1982, Petersen 1982), although Bruland (1989) has suggested that some species of oceanic phytoplankton may have acquired the ability to extract zinc from the high affinity organic ligand which binds up to 98% of the total dissolved zinc in the surface waters of the offshore environment.

In the ocean zinc is usually present in a deficient, or near-deficient, concentration. Free zinc ion in the North Pacific follows an identical vertical distribution to silicate (Bruland 1989), supporting Rueter and Morel's (1981) description of its essentiality for diatoms. The optimal range of zinc for one

coastal species, *Thalassiosira weissflogii*, is only between 10^{-9} to 10^{-11} M (Anderson, et al. 1978) as are the ranges for seven other species of neritic diatoms and coccolithophores (Brand, et al. 1983). The optimum for two oceanic species, *T. oceanica* and *Emiliana huxleyi*, however, is about $10^{-12.3}$ M (Sunda and Huntsman 1992), while in the North Pacific the pZn is only about 12.7 (Bruland 1989), so zinc is clearly a potentially limiting nutrient. Although Sunda and Huntsman (1992) did not find any specific examples of zinc limitation of species within their preferred habitat, nonetheless, it is possible that zinc concentrations may control the distribution of individual phytoplankton species within the ocean (Bruland 1989, Sunda 1988, Sunda and Huntsman 1992).

Zinc apparently so severely limits primary production in the world ocean that a number of phytoplankton species have developed substitute enzymes to use other trace metals when they are zinc deficient (Sunda 1988). Both cadmium and cobalt can be used; replacement with cadmium yields a 90% maximum growth rate for *Thalassiosira weissflogii*. Replacement with cobalt produces a 60% maximum growth rate (Price and Morel 1990). As cadmium is normally considered to be a toxic heavy metal with no known metabolic function and has been widely thought to poison organisms by interfering with their zinc metabolism (Förstner and Wittman 1979), this discovery by Price and Morel may force a reassessment of the physiological utility of this metal (Sunda 1988).

In freshwater zinc toxicity has been observed more often than deficiency. (e.g., Whitton, et al. 1981). Non-heterocyst-forming cyanophytes appear to be more tolerant of high zinc concentrations than are nitrogen fixing cyanophytes or eukaryotic algae (Shehata and Whitton 1981).

However, a lack of zinc may limit growth of natural populations of freshwater phytoplankton (Goldman 1972), and changes in zinc concentrations in natural waters can directly reflect assimilation by phytoplankton as the elegant stoichiometric study done by Reynolds and Hamilton-Taylor (1992) on the spring bloom of *Asterionella formosa* in Windermere demonstrates. Reynolds and Hamilton-Taylor found a number of important characteristics about zinc utilization by freshwater algae. First, up to and through the spring bloom, dissolved zinc concentrations are positively and significantly correlated with phosphate and silicate. Second, after the spring bloom, there is a distinct verti-

cal difference in dissolved zinc with a significantly greater amount present in the hypolimnion of Windermere. Third, the zinc content of *Asterionella* in Windermere is relatively consistent year to year at about $1200 \mu\text{g}\cdot\text{g dry wt}^{-1}$ and the C:Zn stoichiometry remains consistent between years; the same as Sigg (1985) found for sediment trap material in Lake Constance. Fourth, about one-half of the dissolved zinc in Windermere is taken up by *Asterionella* during its spring bloom. Fifth, the bulk of zinc sedimentation is during April and is due to *Asterionella* cells sinking out of the water column. These last two observations partly confirm Collier and Edmond's (1981) Zn flux model for freshwaters. Sixth, the significant biological transformation of zinc is not duplicated for copper as the Cu content of *Asterionella formosa* is only about $45 \mu\text{g}\cdot\text{g dry wt}^{-1}$, and the copper fluxes due to the spring *Asterionella* bloom are only about 10% of those of zinc. That is to say, most of the dissolved copper in Windermere is not involved in biological transformation unlike zinc (in fact, instead of losing mass to the sediments of Windermere as might be expected, about 31 kg of copper are actually liberated during the spring bloom - Figure 6, p.1766).

d. Copper

Copper limitation in natural waters is almost exclusively due to toxicity rather than to an inadequate supply. Although this trace metal is an essential element for plant, algal, and cyanophytic growth, it is apparently almost always present in high enough concentrations as never to be limiting. Rare and limited exceptions do exist however (Wurtsbaugh and Horne 1982). Extra Cu has long been routinely added to control water blooms (Mackenthun 1969, Mulligan 1969, Vallentyne 1974); copper sulfate additions are heavily used for this purpose in one of the study lakes, Oswego. Natural amounts of copper alone may occasionally be enough to prevent nitrogen fixation, hence water blooms (Horne and Goldman 1974), however these are species-specific toxicities which may be due to the high energy requirement of nitrogen fixation by cyanophytes rather than greater Cu sensitivity by these organisms (Wurtsbaugh and Horne 1982, Leland and Carter 1984, Rueter and Petersen 1987).

The relative ability of copper to enter an algal or cyanophytic cell appears to be controlled by the concentration of free copper ion (McKnight 1981, Petersen 1982, Rueter, et al. 1987). Copper often forms strong complexes with or-

ganic materials which leads to annual cycles of free Cu ion concentrations similar to ones caused by extensive biological uptake (Kimball 1973). The relative sensitivities observed between different species of algae and cyanophytes to this metal seems to be due to whether or not the copper can enter the cell and where it is located within the cell (Button and Hostetter 1975; Wood and Wang 1983, Folsom, et al. 1986, Twiss and Nalewajko 1992).

Copper toxicity to diatoms is apparently due to its interference with silicate metabolism (Morel, et al. 1978, Rueter, et al. 1981). Silicate uptake is not inhibited by the free Cu ion as Cu-inhibited diatom cells have higher than normal intracellular pools of silicate; the toxicity may be due to interference with the silicification process as new frustules are aberrant (Rueter, et al. 1981). This interference also affects resting spore formation although additional dissolved silicate reduces the severity, and once formed, the resting spores are resistant to high Cu concentrations (Valente, et al. 1987).

While the biologically driven zinc dynamics during the spring *Asterionella* bloom in Windermere (Reynolds and Hamilton-Taylor 1992) partially confirms the Zn flux model conceptualized by Collier and Edmond (1981), their copper results are in conflict with Collier and Edmond's proposed Cu flux model, despite subsequent verification of it for the ocean (Lyle and Collier 1987). Reynolds and Hamilton-Taylor explain the difference in the biogeochemical cycling of these two metals as being due to the high degree of organic complexation of copper in freshwater while zinc concentrations in these waters are largely as the free ion. Utilization of DPASV (Coale and Bruland 1988, Bruland 1989) during a spring freshwater diatom bloom along with measuring the elemental composition of the phytoplankton could confirm their hypothesis.

e. Cobalt

No evidence exists in the literature for the direct limitation of primary production by cobalt; however, there have been a number of studies which indicate that the Co-containing vitamin B₁₂ may limit the growth of both cyanophytes and diatoms (diatoms - Droop 1970, 1973, Eppley 1977, Patrick, 1977; cyanophytes - Fogg 1973, et al. 1973, Stanier 1973). Indeed, Nolan, et al. (1992) have shown that some species of marine phytoplankton preferentially accumulate Co-cobalamine over inorganic Co. In addition to the requirement

by diatoms and cyanophytes for the Co-containing vitamin B₁₂, chrysophydan microflagellates also require Co (Sandgren 1988), though this requirement may be for vitamin B₁₂ instead.

In lakes, cobalt follows a “typical nutrient” seasonal cycle (Wetzel 1975), implying that its concentration may be controlled by algal uptake. However, Balistrieri, et al. (1992b) demonstrated that this cycle more closely correlates with precipitating manganese oxyhydroxides rather than to phytoplankton uptake. Lee and Fisher (1993) found that the oxidation, and subsequent precipitation of Co, is microbially mediated. Consequently the annual geochemical Co cycle in lakes appears to be biologically driven though not due to the uptake by primary producers. The possibility that low dissolved Co concentrations cause the observed growth limitation of some phytoplankton by vitamin B₁₂ has never been demonstrated; thus, some phytoplankton could be Co, or more likely vitamin B₁₂, limited if microbial oxidation rates greatly exceed microbial transformation rates of Co into vitamin B₁₂ and/or phytoplankton uptake rates of this vitamin were slower than the oxidation rate.

f. Nickel

There have been several published studies which demonstrate the toxicity of nickel to naturally-occurring associations of eukaryotic algae and cyanophytes (Patrick, et al. 1975; Patrick 1978; Spencer 1980; Wood and Wang 1983). These studies have shown clear differences between the various taxa in terms of tolerance to high Ni concentrations. Cyanophytes appear to be the most tolerate and green algae the least (Patrick, et al. 1975; Spencer and Greene 1981); diatoms were more similar in their Ni tolerance to green algae than to the cyanophytes (Patrick 1978; Spencer 1981). No results for other phytoplankton have been published.

Evidence demonstrating possible limitation of phytoplankton growth by an inadequate supply of nickel is less clear. Although Van Baalen and O'Donnell (1978) found a form of *Oscillatoria* which required Ni for growth at about the same time as most of the initial Ni toxicity studies were published, Eskew, et al. (1983) demonstrated that nickel was essential for legumes, and Ni uptake by *Anabaena cylindrica* has been shown to be a metal-specific process which requires energy (Campbell and Smith 1986); much of the proof that insuffi-

cient Ni concentrations can limit phytoplankton growth in natural environments is indirect. Jones and Murray (1984) as well as Bruland (1980) found that nickel is vertically distributed in the northeast Pacific similarly to phosphate and silicate. This suggests that one of its regeneration cycles may be connected to a nutritional requirement of algae for nickel; however, Boyle, et al. (1981) indicated that the Ni:Si regeneration ratio is reduced in areas of intense diatom production. Such a finding, of course, lends support for the importance of Ni toxicity to diatoms, and reduces the significance of the vertical co-variation of nickel with phosphate and silicate. Jones and Murray also have shown that the horizontal distribution of nickel is correlated with resuspension of manganese rich sediments, and not with any biological process. Subsequent to Jones and Murray, Oliveira and Antia (1984, 1986) as well as Price and Morel (1991) have demonstrated that nickel is essential for marine diatoms, and several other major taxonomic groups of marine phytoplankters, when they are grown with urea as their only source of nitrogen. Price and Morel believe that co-limitation due to a lack of nickel and nitrogen in a form other than urea "may naturally exist in oligotrophic waters (p. 1076)." However, documentation of an actual example from a natural environment has not been published.

g. Vanadium

Many natural waters appear to be vanadium deficient as Lee (1983) has demonstrated that an addition of only 20–25 $\mu\text{g}\cdot\text{l}^{-1}$ of V ($\sim 0.4\text{--}0.5\ \mu\text{mol}\cdot\text{l}^{-1}$) can stimulate primary productivity among freshwater phytoplankters; however, this is a narrow optimum, as only 100 $\mu\text{g}\cdot\text{l}^{-1}$ is toxic to many species. Collier (1984) found that V was depleted in surface waters of the North Pacific as might be the case if it limited marine primary production. Both Middelburg, et al. (1988) and Collier (1984) observed that V behaves similarly to phosphate in its vertical distribution, and Middelburg, et al. (1988) found a constant molar ratio of $2.4\cdot 10^{-3}$ for DV/DP in the North Pacific, North Atlantic, and Northeast Indian Oceans. While Middelburg, et al. consistently found more dissolved V than did Collier (1984), they also calculated that the difference could be explained entirely by increased atmospheric inputs to the North Atlantic.

Lee (1983) found that there were major differences in V requirements and sensitivities for different major algal taxa with the growth rate of some dia-

toms being reduced at a V concentration of only $10 \mu\text{g}\cdot\text{l}^{-1}$, while the green alga, *Chlorella*, and the dinoflagellate, *Ceratium hirundinella*, were not affected until concentrations had exceeded $100 \mu\text{g V}\cdot\text{l}^{-1}$ (about $2000 \text{ nmol}\cdot\text{l}^{-1}$) and some cyanophytes had increased growth up to $500 \mu\text{g V}\cdot\text{l}^{-1}$. He also observed large within-division variation in sensitivity to this metal and differences in sensitivity due to water chemistry. These differences in sensitivities are not trivial as Collier has found V concentrations in 11 *apparently* unpolluted Oregon lakes ranging from 0.5 to $108.5 \text{ nmol}\cdot\text{l}^{-1}$ (Collier unpublished data). The maximum found is over half the threshold sensitivity to V for some diatoms based upon Lee's data.

h. Molybdenum

Hutchinson (1957) was the first to hypothesize that molybdenum might be limiting phytoplankton growth in natural waters, and Goldman (1960) found evidence for such limitation in Castle Lake, CA. Molybdenum was subsequently found to stimulate primary productivity in a number of Californian and New Zealand lakes (Goldman 1964, 1972) as well as in a soft water Vermont lake (Allen 1972) and to stimulate nitrate uptake by phytoplankton (Axler, et al. 1980). Dumont (1972) found a seasonal water column Mo cycle and within the phytoplankton which was not apparently significantly affected by sedimentary geochemical processes. Furthermore, species-specific responses to Mo addition were found by Goldman (1972, Jassby and Goldman 1974) which would have been expected on the basis of Tilman's (1982) resource partitioning model.

However, despite the numerous findings by Goldman and his students, widespread Mo limitation has not been demonstrated. Unlike the vertical patterns of Ni and V which are similar to those of major phytoplankton nutrients, Collier (1985) found a uniform vertical profile for Mo in the northeast Pacific, and concluded that "there is no evidence found in the distribution of the form of dissolved molybdate to suggest that it undergoes significant biological cycling analogous to nitrogen or phosphorus. This observation is consistent with a conclusion that the concentration of molybdenum in seawater does not limit primary production (p.1353)."

Subsequent to Collier's paper, much of the published literature on the subject of limitation of marine nitrogen fixation has gone in two different directions. One line of research has focused on the possible role of iron as the limiting nutrient for nitrogen fixation in the world ocean as previously reviewed, while Howarth and Cole have engaged in a debate with Paerl over the role of molybdenum in the marine environment and the significance of the sulfate to molybdate ratio in preventing nitrogen fixation. Since this dispute has implications for possible restrictions on Mo limitation of freshwater phytoplankton, I will now attempt to very briefly summarize the latter disagreement.

About the same time as Collier published his paper, Howarth and Cole (1985) suggested that the high concentrations of sulfate in seawater inhibits the assimilation of molybdate by marine phytoplankton, so reduces nitrogen fixation and nitrate assimilation in seawater, and in a series of articles (Cole, et al. 1986, Howarth, et al. 1988, Marino, et al. 1990, Cole, et al. 1993), attempted to demonstrate their hypothesis. Meanwhile H.W. Paerl and his colleagues have published several studies (ter Steeg, et al. 1986, Paerl, et al. 1987, Paulsen, et al. 1991) which basically attempt to refute these ideas. The most interesting paper of this exchange was Marino, et al. (1990) which demonstrated sulfate inhibition of molybdate uptake and hence of nitrogen fixing cyanophytes in 13 saline Albertan lakes. Their results specifically distinguished between nitrogen fixing cyanophytes and non-nitrogen fixers; the former were strongly affected by the presence of sulfate, the latter were not. Especially important was a demonstration that the $\text{SO}_4:\text{MoO}_4$ ratio could predict how the abundance of nitrogen fixing cyanophytes in a saline lake would differ from a freshwater lake with the same total phosphorus concentration (Fig.3, p. 255). R^2 for this model was 56%.

Pearl's group responded with a demonstration that an obligatory Mo-requiring *Azotobacter vinelandii* strain was not inhibited by sulfate: molybdate ratios eight times higher than found in seawater (Paulsen, et al. 1991). High sulfate concentrations also did not prevent ambient molybdate concentrations from stopping synthesis of two non-Mo requiring nitrogenases, greatly weakened the possibility that marine nitrogen fixers might have specialized in synthesizing non-Mo nitrogenases. Having concluded that molybdate was not limiting *Azotobacter vinelandii* and having failed to find any response to iron in

these experiments as well as ruled out any V-nitrogenases, Paulsen, et al. restated their earlier (Paerl, et al. 1987) conclusion that “organic carbon limitation coupled with oxygen inhibition (is) the key environmental factor” in controlling marine nitrogen fixation rates. However, this study used a non-photosynthetic, non-marine, organism to support their hypothesis that trace metals are insignificant in the process of nitrogen fixation by all nitrogen fixers in the ocean, including autotrophic ones. This appears to be a questionable approach, especially since species-specific responses to molybdenum have been demonstrated (e.g., Goldman 1972, Wurtsbaugh 1988, Cole, et al. 1986).

An interesting interjection into this debate was made by Wurtsbaugh (1988) who analyzed for possible N₂ fixation limitation by Fe, Mo, P, and a sugar, fructose, in two lakes in Utah. In Great Salt Lake only P increased N₂ fixation while fructose significantly *inhibited* it. All three elements stimulated N₂ fixation in East Canyon Reservoir. Wurtsbaugh concluded that both Fe and Mo *could* be important for nitrogen-fixation, but that the SO₄:MoO₄ ratio was not “a critical or reliable determinant for this phenomenon in all systems (p. 128).”

Magyar, et al. (1993) recently reported that Mo in the eutrophic Greifensee, CH, was homogeneously distributed with respect to depth except near the lake bottom where the concentration was lower, similar to what Collier (1985) observed in the Pacific, so they concluded that Mo behaved conservatively in Greifensee.

In summary, there appears to be some evidence to support possible Mo limitation of nitrogen fixing cyanophytes in some lakes, but nothing to support the same phenomenon occurring in the ocean. It is my impression after a careful re-reading of this entire set of papers that the basic questions that Howarth and Cole were asking are “Why aren’t there autotrophic N₂ fixing plankters in the world ocean like there are in inland waters? Does it have anything to do with high sulfate concentrations in the ocean?” Paerl demonstrated that sulfate interference with Mo is not limiting marine N₂ fixation, but he also seems to be claiming that the lack of N₂ fixation in the world ocean is *solely* due to the oxygenated conditions of the marine surface waters and a lack of adequate organic substrates for heterotrophic N₂ fixers. The latter assertion completely ignores a critical point in my opinion; namely, there are photosyn-

thetic organisms which are abundant in inland waters but are uncommon in the ocean and which simultaneously fix nitrogen and liberate oxygen, as well as not needing organic materials. If the world ocean is nitrogen limited, then why aren't these autotrophs more common in the marine environment? What is preventing heterocyst-forming cyanophytes similar to *Anabaena* and *Aphanizomenon* from taking over the tropical oceans? This debate has only removed a few possible explanations, not answered the original question.

3. Distribution of Trace Metals in the Water Column

Before beginning this section, it is important to note that the following biogeochemical processes, except where noted, have been shown to operate across a broad spectrum of lake types (Hamilton-Taylor and Willis 1990). They reached this conclusion through a comparison of different lakes which demonstrated roughly similar proportions (not absolute concentrations) of dissolved materials being retained in different lakes with different water chemistries and the presence of a common sequence of residence times for specific trace metals.

a. Iron

Iron has a very low solubility in oxygenated waters (Anderson and Morel 1982, Drever 1982, Hutchinson 1957, Stumm and Morgan 1970), because it forms iron oxyhydroxides in such waters, siderite (FeCO_3) in waters with a high alkalinity, and, in anoxic waters, iron sulfide (Jacobs, et al. 1985). All of these compounds have low solubility products (Drever 1982, Stumm and Morgan 1970). Consequently, much of the iron present in natural waters occurs as particulate material greater than $12\text{ }\mu\text{m}$ in diameter (Laxen and Chandler 1983, Laxen and Harrison 1981), although these particles may stay suspended in hypolimnetic waters for over two months (Laxen and Chandler 1983). Up to 50% of the total iron present in natural waters exists in dissolved organic and colloidal complexes (Shapiro 1964, Koenings 1976, Urban, et al. 1990). The behavior of this material is pH-dependent. "Organic matter has opposite influences on trace-metal concentrations above and below pH 5. Above pH 5, organic matter enhances the solubility of the mineral phases and thus acts to increase total concentrations of Fe and Al. Below pH 5, organic

matter buffers trace-metal concentrations at a fixed ratio to DOC. Thus total metal concentrations are proportional to DOC ..., but the DOC flocculation process maintains the Fe and Al concentrations well below the limit imposed by mineral solution (p. 1530, Urban, et al. 1990)." Sunlight has been shown to degrade these organic compounds (Anderson and Morel 1982). What little dissolved free ionic iron remaining in oxygenated waters is as Fe(III) (Macalady, et al. 1982).

Iron precipitates out of the epilimnion of lakes and other oxygenated waters largely as Fe oxyhydroxide (Drever 1982, Stumm and Morgan 1970, Urban, et al. 1990) and as FeS in some anoxic hypolimnions (Carignan and Tessier 1988, Stauffer 1986). Under reducing conditions in the hypolimnion of low sulfate, seasonally anoxic lakes, as well as within meromictic lakes (Campbell and Torgersen 1980), Fe is regenerated from surficial sediments and particulate Fe in the hypolimnion (Balistrieri, et al. 1992a, Davison 1981, Morfett, et al. 1988). Most of the reductive remobilization of Fe oxyhydroxides occurs within the top three cm of the sediments (Morfett, et al. 1988). Ferrous iron is vertically transported up through the hypolimnion to the redox boundary where it is oxidized to Fe(III), then forms particulate material. These particles subsequently sink and are re-dissolved lower in the hypolimnion. This phenomenon has been called the "Ferrous Wheel" cycle by Campbell and Torgersen (1980), and has the effect of trapping most of the iron within the lakes containing such a boundary in the water column (Davison, et al. 1982). The ocean lacks a similar cycle. "The vertical distribution of dissolved Fe in the ... Pacific appears to be controlled by particle ... scavenging ... throughout the water column, uptake and removal from the photic zone, and little or no regeneration with depth (p. 39, Landing and Bruland 1987)."

The geochemical behavior of iron and other trace metals has been followed in detail in Lake Sammamish by Balistrieri, et al. (1992a, 1992b). Flux rate calculations indicated that there were adequate amounts of both oxygen and reduced metals in the hypolimnion to produce Fe and Mn oxide precipitation in the particulate zone of the hypolimnion (Balistrieri, et al. 1992a). While FeS formation and precipitation was thermodynamically possible in the very deepest parts of this lake, it was probably not a major cause of Fe precipitation because sulfide was not released from lake sediments until over 20 weeks

after stratification began, while oxygen began to decline immediately after stratification. Furthermore, during the later sulfidic stagnation period (September to November), although particulate Fe peaked at depths where the sulfide concentration began to increase, there was an insufficient supply of HS^- in the particulate zone to produce the observed concentrations of particulate Fe (Balistrieri, et al. 1992a). The particulate material collected on filters from the deepest sampling location (28-29 m) during this period was initially black, but turned orange-red upon long-term exposure to air, suggesting that FeS may have formed in the very deepest part of the lake, though it was not apparently a major share of the particulate Fe present. While the fall IAP_{CO_3} values (the ion activity product for carbonate) in Lake Sammamish were very close to the solubility product for siderite, analyses of the suspended particles indicated an absence of this compound (Balistrieri, et al. 1992a).

The low solubility of iron and its chemical interactions with other trace metals through adsorption, coprecipitation, and reductive dissolution processes partially drives the aqueous chemistry for four of the trace metals studied here as well as several others which were not investigated in this research (Balistrieri, et al. 1992a, 1992b). The specific metals impacted by Fe cycling are Mn, Co and V to some extent, and, indirectly through its interaction with Mn, nickel.

The principal biological effect of the aqueous chemistry of iron is to reduce its availability greatly. However, the form that iron occurs in is probably not very important in terms of its uptake by phytoplankton since some species have been shown to utilize colloidal Fe up to a diameter of 350 Å (De Haan, et al. 1985). Nor is the oxidation state of iron likely to be critical as some diatoms have been found to use Fe(III) specifically (Anderson and Morel 1982).

b. Manganese

Manganese is more soluble than iron in natural waters (Stumm and Morgan 1970, Delfino 1968), and its total concentration is second only to iron in both freshwater lakes and the ocean. Differences in the redox potential of these two metals result in significant temporal and spatial differences in their distribution (Balistrieri, et al. 1992a, Landing and Bruland 1987). Manganese is present in natural waters primarily, but not exclusively, as the dissolved Mn^{2+}

ion and as particulate MnO_2 (Morgan and Stumm 1965, Stumm and Morgan 1970). Organic complexes are not important components in the total dissolved concentration of this metal (Urban, et al. 1990). The Mn oxidation rate in lake epilimnions is strongly modified by pH (Delfino and Lee 1968, 1971) and temperature (Tipping 1984); however, oxidation is very slow at pHs typical of most natural waters (Sunda and Huntsman 1990). Dissolved Mn resides in the oxic euphotic zone much longer than does iron (weeks vs. hours) because of its slower reaction rate with oxygen (Stumm and Morgan 1970, Delfino 1968, Delfino and Lee 1968, Balistrieri, et al. 1992a). High concentrations are also maintained longer due to the fact that Mn oxides undergo a significant amount of photoreduction to Mn^{2+} (Sunda and Huntsman 1985, 1988).

Manganese oxidation is biologically mediated (Tipping 1984); but it is not associated with phytoplankton (Laxen and Chandler 1983). Reaction rates are greatly increased by microbial activity (Chapnick, et al. 1982, Kepkay 1985, Stabel and Kleiner 1983, Sunda and Huntsman 1988, 1990, Tebo, et al. 1984). Sunlight apparently inhibits these Mn-oxidizing bacteria (Sunda and Huntsman 1988), and large diel variations in the concentrations of both particulate and dissolved Mn (in opposite directions) have been observed (Sunda and Huntsman 1990). The photoinhibition of Mn-oxidizing bacteria appears to be a more important mechanism for causing diel variations than direct photoreduction (Sunda and Huntsman 1990). Both Chapnick, et al. (1982) and Kepkay (1985) found evidence for microbially-controlled Mn oxidation in lakes. A model of Mn cycling in a seasonally anoxic lake (Johnson, et al. 1991) also produced rates supporting the presence of microbial oxidation in the study lake, though the model failed to duplicate the particulate Mn peaks found in Greifensee. The surface maxima of both dissolved and total Mn in the ocean found by Landing and Bruland (1987) is probably partially due to this interaction of sunlight and Mn-oxidizing bacteria (Sunda and Huntsman 1990). These bacteria are less numerous in the open ocean than in coastal waters (Sunda and Huntsman 1990). Equivalent distribution studies have not been systematically done in lakes, although Urban, et al. (1990) did not find strong evidence for Mn-oxidation in their oligotrophic Nova Scotia lakes, while Johnson, et al.'s eutrophic Swiss lake clearly supported a large population of Mn-oxidizing bacteria, Chapnick, et al.'s work took place in Lake Oneida, another eutrophic lake, and

Kepkay's study site was in Lake Charlotte, NS, which has very high concentrations of dissolved organics present. (It should be noted, however, that Urban, et al. did suggest that the absence of Mn-oxidizing bacteria in their lakes might be due to a low mean pH.) Sunda and Huntsman (1990) hypothesized that the difference between the open and neritic ocean densities of these bacteria was due to the concentration of organic substrates; a similar phenomenon seems to occur in lakes based upon the above examples.

In anoxic waters the limiting compounds on Mn solubility are rhodochrosite, or MnCO_3 , (Delfino and Lee 1968, 1971, Robbins and Callender 1975) and MnS (Brezonik, et al. 1969, Delfino and Lee 1968, 1971). Neither have been found to be important controls on Mn solubility (Balistrieri, et al. 1992a, Urban, et al. 1990) other than in hard water, high alkalinity lakes (Delfino and Lee 1968).

Natural weathering of exposed rock in the watershed is the chief external source of manganese for most lakes (Urban, et al. 1990). Catchment area, not natural vegetation cover nor in-lake processes, is the primary control upon manganese concentrations in oligotrophic lakes (Urban, et al. 1990). Dissolved Mn in all lakes is regenerated by particulate Mn redissolving in the hypolimnion as it settles out before reaching the sediment-water interface (Balistrieri, et al. 1992a, Davison 1981, Landing and Bruland 1987), and by reduction of superficial sediments (Stauffer 1986). Cycling by manganese between the dissolved and particulate components occurs higher in the water column than does the equivalent iron exchange (Balistrieri 1992a). Exchangeable (or pore-water) Mn is very high in superficial lake sediments (Tessier, et al. 1980) and hypolimnetic concentrations have been demonstrated to be regulated by ion exchange with the sedimentary porewaters (Anderson, et al. 1987, Santschi, et al. 1986). Oceanic Mn demonstrates a similar abiological behavior. Flux rates from continental shelf sediments are adequate to sustain the high dissolved Mn concentration zone in surface waters of the ocean and the available evidence suggests that "each Mn atom (is) recycled from the shelf sediments to the water column many times before export to the open sea (p. 1244, Johnson, et al. 1992)."

Manganese remobilization from lake sediments is strongly linked with P, as both elements possess the same vertical profile (Stauffer 1986), nickel (Balistrieri, et al. 1992b, Kepkay 1985), and cobalt (Balistrieri, et al. 1992b).

The vertical Mn profile in the ocean resembles that of iron, except for the presence of a near-surface maximum. Below that is a shallow zone of low concentration, a maximum which coincides with the oxygen minimum, and very low values in the deep ocean (Landing and Bruland 1987). Diffusion of Mn from oceanic sediments is not believed to be the source of the subsurface maximum as benthic flux rates are too low (Johnson, et al. 1992). Eutrophic lakes tend to have strong seasonal patterns with high Mn concentrations in the summer hypolimnion and modest concentrations throughout the water column, including the epilimnion during the fall or early winter turnover (Balistrieri, et al. 1992a, Delfino 1968).

c. Zinc and Copper

Redox transformations by iron and manganese have not been found to control the concentrations of either dissolved zinc or copper in natural waters (Morfett, et al. 1988) in opposition to long and widely held opinions (e.g. Jenne 1968). "If hydrous iron and manganese oxides provide an important trace metal removal mechanism, trace metal concentrations could be expected to vary during periods of iron and manganese remobilization. Thus seasonal accumulation of soluble Fe(II) and Mn(II) in the anoxic hypolimnion could be expected to correspond with elevated trace metal concentrations. These effects were not observed. ... Interfacial trace metal concentrations ... showed a significant decline during this period. ... (S)easonal variations of dissolved trace metals are not appreciably influenced by redox driven dissolution of iron and manganese oxyhydroxides (Morfett, et al. 1988, p. 109)." The role of insoluble sulfides of zinc and copper were also examined by Morfett, et al. (1988) and while that trace metal sulfides were supersaturated with respect to their chemical equilibrium value, there were no water column minima observed during the anoxic period in Esthwaite Water. Thus, it appears that sulfides are not an effective control on trace metal concentrations in this eutrophic, soft water lake. Nor did they find the lake sediments to be a significant source for these two trace metals. Morfett, et al. concluded that external loadings appear to be

the major source of these metals for Esthwaite Water, and that biological uptake and release were important internal recycling routes for both copper and zinc in this low alkalinity, seasonal anoxic lake.

Variations in water column zinc concentration in unpolluted environments seem to be exclusively controlled by two factors, utilization by diatoms for silicate uptake and metabolism, and the concentration of organic ligands with high, relatively specific, Zn affinities (Balistrieri, et al. 1992b, Bruland 1980, 1989, Reynolds and Hamilton-Taylor 1992). The molar concentration of total acid-soluble Zn in most natural waters measured equals between 5.4 and 5.6 $\times 10^{-5}$ the molar concentration of reactive silicate (Balistrieri, et al. 1992b), while up to 98% of the dissolved Zn, at least in the open ocean North Pacific, is complexed with an organic ligand which is specific for this trace metal (Bruland 1989). The good correlation between dissolved Zn and silicate only means that this is the driving mechanism for Zn concentrations in the water column, not that other phytoplankters don't require and utilize Zn. This relationship was first observed in 1972 (Wilson 1978).

The only complications in describing the distribution of zinc in natural waters are the roles of anthropogenic Zn inputs and acidification. These processes are frequently, but not always, correlated (Henriksen and Wright 1978). Severe acidification drastically changes Zn behavior in natural waters. When iron oxyhydroxides are available in acidified waters, zinc precipitates onto them (Johnson 1986); where such compounds are absent and the pH is <5.5 , water column Zn behaves semi-conservatively (White and Driscoll 1987a). The latter pattern is probably due to a pH-caused inactivation of organic ligands and suppression of diatom production (Schindler 1985), or increased resolution of zinc from diatoms sinking out of the water column (Santschi, et al. 1986).

Copper is the cation least affected by iron and its co-precipitators (Balistrieri, et al. 1992b). Nor does copper correlate with any nutrient, at least in the ocean (Jones and Murray 1984). Most of the dissolved Cu present in natural waters is in the form of organic complexes along with much smaller amounts of inorganic ions (Allen, et al. 1970, Coale and Bruland 1988, McKnight 1981, Wagemann and Barica 1979, Wilson 1978), although it can also form complexes with hydroxide, carbonate, phosphate, and ammonia (Benjamin and Honeyman 1992, Sanchez and Lee 1978). A yearlong study by Kimball (1973)

in a soft water Massachusetts pond demonstrated an annual cycle for ionic Cu which reflected seasonal uptake by the biota and showed a failure by conservative ions in the water column or other chemicals entering the pond from the watershed to suppress the amount of ionic Cu regenerated during the fall and winter from decomposition. However, in contrast, Cu solubility in an alkaline Wisconsin lake was controlled by dissolved carbonate under oxic conditions and by sulfide under anoxic conditions (Sanchez and Lee 1978), thus conservative water chemistry can have a small impact on the solubility of this trace metal.

Dissolved copper associated with organic materials is not very biologically available (McKnight 1981), and dissolved organic Cu is completely unavailable for any interactions with dissolved S (Benjamin and Honeyman 1992). In the ocean, dissolved Cu is significantly enriched in water over the continental shelves (Knauer and Martin 1973), apparently due to the greater amounts of organic material present (Boyle, et al. 1981). The organic ligands which complex with this metal seem to be mainly produced by planktonic algae (Xue and Sigg 1993).

The large amounts of copper sulfate added as an algicide do not remain in the water column of most lakes for very long (McKnight 1981) as it appears to be rapidly converted into covellite (CuS) or chalcocite (Cu_2S). Lake sediments serve as the primary sink for the added copper (Sanchez and Lee 1978).

d. Cobalt and Nickel

Dissolved cobalt follows a very similar pattern to iron and manganese (Balistrieri, et al. 1992b). In Lake Sammamish, it increases greatly in the hypolimnion during the summer stagnation period. According to Balistrieri, et al (1992b), "(b)ottom water inventories, concentrations, and speciation of Co are strongly linked to the seasonal cycle of the lake and the cycling of Mn (p. 531)." Cobalt, like Mn, will also rediffuse into the water column if the water has been acidified (Santschi, et al. 1986). Again like Mn, Co oxidation has recently been shown to be driven by microbial activity which may be photoinhibited (Lee and Fisher 1993). Lee and Fisher (1993) also ruled out both preferential adsorption of Co(II) onto Mn oxides and chemical oxidation of Co(II) by Mn oxide as alternatives to microbial oxidation. Particulate Co, however, appears to correlate better with particulate Fe instead of particulate Mn, apparently

because particulate Fe scavenges part of the dissolved Co in the hypolimnion after it has been liberated during anoxia (Balistrieri, et al. 1992b), or possibly because the Co-oxidizing bacteria are associated with particulate Fe.

It is believed, but has not been tested, that most dissolved nickel in lakes is present as either an ion or in a organically-complexed form, similar to copper (Snodgrass 1980). Dissolved Ni covaries with both phosphate and silicate in the ocean (Boyle, et al. 1981, Bruland 1980, Jones and Murray 1984). However, the relationship with silicate decreases in the subarctic northeast Pacific due to a sharp increase in diatom productivity combined with an increase in silicate regeneration relative to nickel (Boyle, et al. 1981). The nickel-silicate relationship was not found in Lake Sammamish (Balistrieri, et al. 1992b), the only freshwater location where this hypothesis has been tested. The summer anoxic conditions in this lake caused a small increase in dissolved Ni in the hypolimnion. The vertical profiles of dissolved Ni suggested a linkage between Mn and Ni (Balistrieri, et al. 1992b), and Ni has been shown to be strongly bound to the same microbially-formed particles as Mn (Kepkay 1985), providing a mechanism for the observed linkage. Hem, et al. (1989) found that these bacterially-generated particles can reduce the dissolved Ni concentration far below predicted oxide or hydroxide equilibrium values. Tessier, et al. (1985) showed that Ni can be scavenged by iron oxyhydroxide particles and Jenne (1968) claimed that the hydrous oxides of Fe and Mn are the principal control on Ni solubility. However, Balistrieri, et al. (1992b) found little evidence to support the proposed role of iron as what little particulate Ni present in Lake Sammamish did not behave similarly to particulate Co which is scavenged by particulate Fe, nor to the particulate Fe itself.

e. Vanadium and Molybdenum

Molybdenum (Chapell 1973) and vanadium (Lee 1983). are present in most natural waters as anions instead of cations. At pHs between 4 and 13, dissolved V is primarily present in freshwater as HVO_4^{-2} and $\text{H}_2\text{VO}_4^{-1}$ with between 1 and 5% as the vanadyl cation VO^{2+} , mostly due to chelation with "humic" acids (Lee 1983, also see Figure 1a of Wehrli and Stumm 1989, p. 70). Dissolved V is believed to chemically behave much like dissolved P (Collier 1984, Middelburg, et al. 1988, Shiller and Boyle 1987, Wehrli and Stumm

1989). The normal range of dissolved V in freshwater is between 2 and 20 $\text{nmol}\cdot\text{l}^{-1}$; in the ocean it is between 20 and 60 $\text{nmol}\cdot\text{l}^{-1}$ (Lee 1983). Collier (1984) found dissolved V concentrations between 30 and 40 $\text{nmol}\cdot\text{l}^{-1}$ at three stations in the open Pacific; the lowest concentrations occurred in the surface layers. Oceanic inputs are apparently largely riverine (with a mean concentration of 15 $\text{nmol}\cdot\text{l}^{-1}$ - Shiller and Boyle 1987) and atmospheric. The surface depletion in the ocean is not due to redox scavenging (Collier 1984). Biogenic uptake is probably responsible for the oceanic depletion (Collier 1984, Lee 1983, Middelburg, et al. 1988). Either biogenic uptake or absorption onto Mn and Fe oxyhydroxides (Wehrli and Stumm 1989) appears to control dissolved V concentrations in lakes.

Very high concentrations of vanadium exist in petroleum (Charles and Norton 1986, Wehrli and Stumm 1989). When oil or other fuels are burned, the vanadium present forms V_2O_5 which is highly soluble in water (Lee 1983). Petroleum combustion is regarded as the primary source of V in freshwater at present (Charles and Norton 1986, Charles, et al. 1987).

Dissolved molybdenum averages about 107 $\text{nmol}\cdot\text{l}^{-1}$ in the northeast Pacific Ocean (Collier 1985) and between 1 and 100 $\text{nmol}\cdot\text{l}^{-1}$ in lakes (Howarth, et al. 1988, Magyar, et al. 1993). It is present under oxygenated conditions solely as the anion, MoO_4^{2-} (Kaback and Runnells 1980, Magyar, et al. 1993). Dissolved molybdate behaves conservatively in both the ocean (Collier 1985) and in eutrophic lakes (Magyar, et al. 1993). The residence time of Mo in the water column of Greifensee is close to that of water (365 days vs. 408 for the water). Biological uptake in the ocean and in eutrophic lakes does not seem to be an important control of molybdate concentration nor is chemical precipitation a large factor (Collier 1985, Magyar, et al. 1993). Biological uptake may be important in some oligotrophic inland waters however (Goldman 1960, 1972, Marino, et al. 1990).

The geochemical controls on Mo solubility have only recently begun to be studied in lake waters due to the low concentrations present (Magyar, et al. 1993). The minimum concentrations of Mo(VI) in Greifensee were found in the bottom waters during the fall, 3.8 $\text{nmol}\cdot\text{l}^{-1}$ (the typical concentration in this lake for the rest of the year and in the surface waters during this period was about 5.5-6.0 $\text{nmol}\cdot\text{l}^{-1}$). No specific mechanisms for the hypolimnetic losses of

this metal were discovered by Magyar, et al. (1993) as this minimum was not due to the formation of a Mo-sulfide in the water column, and the flux of Mo in settling particles did not significantly correlate with Fe, Mn, Ca (i.e. sedimenting calcium carbonate), or C (i.e., organic material). They proposed 1) coprecipitation of MoS_3 on FeS in sedimentary porewater, 2) uptake by nitrate-reducers at the sediment-water interface, and/or 3) reduction to Mo(V), followed by complexation by organic materials in the superficial sediments. All three possible mechanisms could cause a sink at the sediment-water interface with Mo being transported to this boundary layer by turbulent diffusion.

Up until Magyar, et al.'s paper, much of the knowledge of Mo transport and speciation in freshwater was limited to theoretical discussions of its physical chemistry. A summary of this information, derived from the tables of Wagman, et al. (1982), is compiled in an Eh-pH diagram (Figure 1). If this figure has been interpreted correctly, then it appears that sulfur may be part of the ultimate control on freshwater Mo concentration as Magyar, et al. and Howarth and Cole have suggested. Nevertheless, currently this must be considered as unproven.

4. Distribution of Trace Metals within Sediments

a. Total Elemental Distribution

The typical elemental composition of lake sediments is divided into five groups, major elements, carbonate elements, nutrients and organic material, mobile elements, and trace elements (Håkanson and Jansson 1983). Si, Al, K, Na, and Mg oxides comprise nearly 80% of the sediment matrix, while carbonates, nutrients and organic materials, and the mobile elements of Fe, Mn, and S together make up about 20%. Trace elements such as Hg, Cd, Pb, Cu, Zn, Ni, Cr, Ag, V, etc. usually comprise less than 0.1% (Håkanson and Jansson 1983).

Sedimentary iron has been shown to be highly associated with oxyhydroxides and carbonates in oxic waters (Stumm and Morgan 1970, Hongve 1974, Drever 1982). It also frequently combines with phosphate as does Mn (Bortleson and Lee 1974, Delfino, et al. 1969, Stumm and Morgan 1970) and with S

Figure 1. Theoretical stability diagram for the aqueous Mo-S system.

(Jacobs, et al. 1985). There is a very strong reaction between Fe and S in natural waters, and in aerobic, but acidic, lakes, Fe sulfide is the primary source of S to the sediments (Carignan and Tessier 1988). Both Fe and Mn undergo redox dissolution and reprecipitation in the superficial layers of sediments in aerobic lakes (Sasseville and Norton 1975) as well as within meromictic lakes (Campbell and Torgersen 1980). The redox boundary where it occurs above the sedimentary-water interface has a significantly different impact upon these two metals as ferrous Fe is vertically transported up to where it is oxidized into Fe(III), then sinks and is redissolved in the "Ferrous Wheel" cycle of Campbell and Torgersen (Balistrieri, et al. 1992a, Davison, et al. 1982). Consequently iron is largely trapped within lakes containing such a boundary. However, Mn strongly contrasts with iron in both Lake Sammamish and Esthwaite Water as the manganous ions which reach the sedimentary surface during the winter are rapidly reduced and released into the overlying water column with less than 10% of the winter total being permanently accumulated in the sediments (Davison, et al. 1982). Furthermore during the summer, due the anoxic hypolimnions of these lakes, little or no Mn reaches the sediments at all (Balistrieri, et al. 1992a, Davison, et al. 1982).

Another difference between the two most abundant trace metals in this study may be the role of microbial activity. Several researchers have demonstrated that bacteria mediate the oxidation rate of manganese in freshwater (Chapnick, et al. 1982, Kepkay 1985, Stabel and Kleiner 1983), while no published evidence for bacterial oxidation of iron was found. It is now known that naturally-formed lacustrine MnO_x exists in two separate forms (De Vitre, et al. 1988), possibly due to its two different origins, i.e., microbially and through the redox geochemical reaction.

A third difference is the extent to which the particulate forms of these metals scavenge other trace metals. The precipitating ferric oxyhydroxides scavenge other metals, including Ca, Mg, Ba, and K (Sholkovitz and Copland 1982a) as well as Mn, Co, and V (Balistrieri 1992b, Delfino 1968, Stumm and Morgan 1970, Wehrli and Stumm 1989). Until recently Mn was thought to coprecipitate both Co and Ni (Balistrieri 1992b); however, new information suggests that much of the particulate Co is formed by bacterial activity independent of Mn-oxide formation (Lee and Fisher 1993), leaving only Ni as co-

precipitating with Mn-oxides. This reaction is thought to be bacterially mediated as well (Balistrieri, et al. 1992b, Kepkay 1985, Hem, et al. 1989). To summarize this difference, Fe scavenges other metals directly, while Mn coprecipitation of other metals appears to be microbially controlled, and is possibly just coincidental rather than causal.

In high alkalinity lakes both Fe and Mn form metal carbonates with low solubility products (Stumm and Morgan 1970). Robbins and Callender (1975) developed a kinetic model for the formation of rhodochrosite, or MnCO_3 , with a calculated rate constant of about one year. Although their model works in both Lake Michigan and the Arctic Ocean basin and can handle anthropogenic inputs, it is non-functional in low alkalinity lakes with low concentrations of carbonate such as predominate in this study.

Dissolved zinc precipitates to lake sediments by one of three routes. Zinc can form a precipitate when dissolved organic Zn complexes react with dissolved sulfide (Hallberg, et al. 1980). This reaction can also take place within the pore water of the top two-three cm of sediment of acidified lakes (Carignan and Tessier 1985). However, the precipitation reaction is not due to the acidity because Santschi, et al. (1986) and Tessier, et al. (1989) found that sedimentary Zn diffuses back into the water column when the water has been acidified to a pH of 4.8. Also, although dissolved Zn precipitates quickly in the presence of sulfide, it has not been shown to be directly part of the redox cycle so important for Fe and Mn precipitation (Jacobs, et al. 1985). The second route is via sorption onto Fe oxyhydroxide particles. Tessier, et al. (1989) constructed a partitioning model of Zn in the water column and sediments. They concluded that sorption processes onto naturally-occurring Fe oxyhydroxide apparently control the dissolved free ion concentration above a pH of 7 as dissolved Zn is highly undersaturated with respect to Zn(OH)_2 , ZnCO_3 , and ZnSiO_3 . This undersaturation precludes the possibility that solubility equilibria with solid phases are the main mechanism for controlling dissolved Zn concentrations. The third route is through incorporation into algal biomass and sedimentation of dead cells. Algal zinc can be a major source of sedimentary Zn (Reynolds and Hamilton-Taylor 1992, Salomons and Mook 1980, Sigg, et al. 1987).

Copper is a relatively inert metal with respect to sedimentary processes, and, by-and-large, Cu is not retained in lakes via sedimentation (Hamilton-

Taylor and Willis 1990). The copper that is incorporated into both oceanic and lacustrine sediments appears to mainly originate as biological material (Hamilton-Taylor, et al. 1984, Kerfoot, et al. 1994, Lyle and Collier 1987, Sigg, et al. 1987), or as sulfide during periods of anoxia (Balistrieri, et al. 1992b), although a relatively small amount of dissolved Cu in the water column is actually taken up by biological activity (Reynolds and Hamilton-Taylor 1992). Copper does not appear to be co-precipitated by Fe oxyhydroxides (Balistrieri, et al. 1992b) or by manganese oxidation (Kepkay 1985). Nor is the carbonate concentration effective in regulating dissolved Cu concentrations as calcium carbonate is not an efficient carrier material for either copper or zinc (Sigg, et al. 1987) and copper carbonate precipitation seems to occur only in very high alkalinity lakes (Sanchez and Lee 1978). Moreover, when Cu is present only in soluble organic complexes, it can not be precipitated by microbiological action (Kepkay 1985) or by sulfide (Hallberg, et al. 1980). Once incorporated into the sediments however, Cu is not liberated again by changes in redox condition as occurs with Fe and Mn (Sakata 1985), or Co (Balistrieri, et al. 1992b). Recycling of sedimentary Cu, Ni, and Zn is primarily tied to the degradation rate of organic material in both the ocean (Westerlund, et al. 1986) and freshwater (Hamilton-Taylor, et al. 1984). Porewater Cu appears to be lost from the sediments only in predominantly inorganic environments (Kerfoot, et al. 1994).

Elevated concentrations of copper in lake sediments are typically caused by human activities, either by Cu mining in the watershed (Davison, et al. 1985, Kerfoot, et al. 1994), use of CuSO_4 as an algicide (Sanchez and Lee 1978), or by pollution discharges either through the air (Galloway and Likens 1979, Henriksen and Wright 1978, Charles and Norton 1986, Ochsenein, et al. 1983) or directly into the water body (Nriagu, et al. 1979, Kerfoot, et al. 1994).

Cobalt possesses the same geochemical behavior as Fe with respect to redox cycling and S (Balistrieri, et al. 1992b, Cornwell 1986, Hesslein 1987, Jacobs, et al. 1985, Sundby, et al. 1986). Consequently similar sedimentary patterns have been observed with Co as for Fe (Cornwell, 1986, Jacobs, et al. 1985), excluding the porewater fraction (Sundby, et al. 1986).

It has been hypothesized that nickel in lake sediments should reflect the Ni content of the bedrock of the watershed (Snodgrass 1980). No study has

actually verified this idea, though Ni concentrations in riverine sediments reflect their bedrock of origin (Snodgrass 1980). The primary mechanism for Ni sedimentation appears to be bacterially-mediated co-precipitation with Mn (Balistrieri, et al. 1992b, Kepkay 1985, Hem, et al. 1989). High concentrations of sedimentary Ni in lakes are typically correlated with airborne pollution (Nriagu, et al. 1982, Snodgrass 1980).

There have been no published studies as to the characteristics of vanadium in sediments despite a number of measurements of its total concentrations. The normal V concentration in sandstone and limestone is 20 ppm; in shale the average is 135 ppm (Lee 1983). The only published investigation of the geochemistry of its formation was that of Wehrli and Stumm (1989). They demonstrated that, under reducing conditions, the vanadyl cation will be absorbed on to oxide surfaces, and suggest that the commoner vanadate anion may be absorbed by hydrous oxides of Mn and Fe, much as phosphate is in some lakes (Stumm and Morgan 1970). However, the major sedimentary form(s) of V remain(s) unknown, and the role of Fe and Mn co-precipitation of vanadate in oxygenated waters needs to be experimentally verified.

Molybdenum is scavenged from the water column by Mn oxides in both lakes and in the ocean. It possessed a similar vertical distribution to Mn in the sediments of the one lake where it had been profiled (Cornwell 1986). The major sedimentary form(s) of this metal have not been identified.

b. Fractionated Distribution

Early in the study of sedimentary metals the question arose of how were the elements partitioned among the different components (Förstner and Wittmann 1979). There were two driving mechanisms for this question, geochemical characterization and biological availability, particularly in polluted environments. Initially the question was porewater metal concentrations vs. concentrations in the solid phase and the transfer rates for different metals between these two phases (Callender 1975 personal communication, Förstner and Wittman 1979), however, as the questions of metal origin and bioavailability became more important, then fractionation of the solids became more detailed. One long-used approach to solid fractionation was to separate sedimentary components on the basis of particle size, and then to analyze each

size class. Except to determine that most of the biologically available metals were in the smaller size fractions, this was not a particularly useful approach, so chemically-based fractionation eventually replaced particle size determination (Förstner and Wittmann 1979, Håkanson and Jansson 1983). One chemical technique developed quite early and still preferred by the U.S. EPA (Dunnette 1983) is a single extraction with hot 3N HCl. This procedure removes almost everything labile from sediments which might be biologically available, yet does not dissolve the primarily lithogenic silicates. It also does not dissolve most organics or compounds which a strong base might liberate (Engstrom and Wright 1984, Tessier, et al. 1979). Consequently more elaborate schemes, based upon the general composition of sediments, were gradually developed (for a review of the history of these procedures and descriptions of them, see Tessier, et al. 1979 and Håkanson and Jansson 1983). The underlying basis for the idea of sequential fractionation was that sediments are made up of a few major chemical components, i.e., of Fe and Mn oxides and oxyhydroxides, of carbonates, of organics, of sulfides, and of non-reactive silicates, and so the questions were first, where are the other metals sequestered, and second, how can one or more of the components be analyzed separate from the others. These questions eventually resulted in the idea of sequential extraction.

One of the first documented successful sequential fractionation procedures was that of Gupta and Chen (1975). They studied eight metals, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, distributed in eight fractions taken from polluted marine sediments. The fractions studied were non-oxygenated interstitial water, simple solubility of solids, exchangeable ions, carbonates, easily reduced Fe and Mn oxides, organic and sulfides, moderately reducible iron oxide, and the lithogenic, or residual, fraction. Their organics+sulfide and residual fractions were the same or very similar to the procedures used here for the same fractions.

Tessier, et al. (1980), developed their now-widely used sequential fractionation technique, then first used it to study trace metal speciation in sediments of two Quebec rivers. The metals studied included Fe, Mn, Zn, Cu, Co and Ni. They found that only about 4.3% of the Fe was present as organics + sulfides while less than 0.01% was found in the exchangeable fraction but a large part of the sedimentary Mn occurred as exchangeable metal, though only 1.5% was

associated with organic material. About 5% of the Zn was present as organics+sulfides while over 40% of the Cu was present in that form. Only 12% of the Co, and 5% of the total Ni present existed in the organic fraction.

Subsequently to this paper, Tessier, et al. (1984) studied the uptake of Fe, Mn, Zn, and Cu by a freshwater mollusc, *Elliptio complanata*, near a mining area. They found that the Cu and Zn concentrations in various tissues did not relate to total metal concentrations in the sediments, but rather to one of the more easily extracted fractions. For Zn, the best predictor was the ratio of organics to oxides; for Cu, it was the sum of all metals other than the organic and residual fractions.

As the concept of sequential fractionation gained support among other researchers (e.g., Evans, et al. 1988, Moore, et al. 1988, Samanidou and Fytianos 1987), it also acquired critics (e.g., E.A. Jenne 1987 PSU ESR seminar) and Tessier's group continued to refine their methodology. The two major (and related) problems of concern were potential readsorption during the sequential extraction and the fact that by changing the sequence of extraction, there could be a difference in resulting product. Tessier and Campbell (1987, 1988) responded to these potential problems by acknowledging that reabsorption could be a problem but that sequential metal extraction fractions are operational definitions, not discrete identities. However, they also observed that bioavailability of trace metals is clearly not related to total sedimentary concentrations and maintained that studies of metal distributions under natural conditions were better predictors of metal distributions and biological uptake than were studies using artificial sediments with doped fractions in the laboratory. Their subsequent research (Belzile, et al. 1989) clearly demonstrated that the feared readsorption of trace metals during sequential extraction was greatly overestimated, especially when the standard addition spikes were at a concentration similar to the natural material. Belzile, et al. also demonstrated that adding large spikes or spikes which are not in a state of chemical equilibrium to sediments resulted in a redistribution of the spike throughout several phases due to the dynamics of the system being studied. Small spikes added to natural sedimentary mixtures have a slower redistribution rate, so when the recovery efficiency of the method was tested, they achieved a rate of recovery

within experimental error in nearly all cases (the sole exception that they found, lead associated with carbonates, is not a problem in this research).

It is my opinion, based upon these papers (and my limited experience), that well chosen sequential extractions provide a highly functional separation of sedimentary components, and that such operational definitions may be thought of as analogous to how P is measured in natural waters. That is to say, the identity which we think of as dissolved inorganic P is actually filterable (usually known as “soluble”) P which reacts to the molybdate blue test, i.e. the measured P is really soluble reactive (SRP), not dissolved inorganic. In both cases, what we say we are measuring and what we are actually measuring are two distinctly different, but overlapping, identities and much of the argument is actually over how good of an overlap is present. For dissolved inorganic phosphate, the functional test used has been proven to be highly useful; although the sequential fractionation test for sediments has not been as extensively analyzed or used, to date it also appears to be functionally quite useful.

c. Some Reports of Atmospheric Deposition

Lake sediments provide a record of past changes in the air and water sheds of the lake. Much of what we know about acid rain and heavy metal pollution in aquatic environments has been learned from studying lake sediments. Lake sediments can also provide information as to the rate of cultural eutrophication (Förstner and Wittmann 1979, Håkanson and Jansson 1983) and land use changes have been shown to cause changes in sedimentary trace metal deposition as well (Davison, et al. 1985, Rippey, et al. 1982). However, vertical changes of many trace metals in lake sediments appear to be mainly due atmospheric deposition (Charles and Norton 1986).

Acid rain frequently causes changes in trace metal concentrations within lake sediments (Charles and Norton 1986, Charles, et al. 1987), although frequently the change is only an increase near the surface of the sediment-water interface due to remobilization (Carignan and Nriagu 1985, Carignan and Tessier 1985). Acid rain is also often associated with increased atmospheric inputs of trace metals (Charles and Norton 1986, Davis, et al. 1983, Galloway and Likens 1979, Norton, et al. 1978), although there are a number of examples of direct increases due to atmospheric deposition in the absence of acid rain

(Baron, et al. 1986, Johnson, et al. 1986, Johnson 1987, Ochsenbein, et al. 1983, Nriagu, et al. 1979). The following set of examples demonstrate a common pattern among the metals possessing clear vertical changes.

Lead, copper, zinc and vanadium have been shown to increase in areas receiving air polluted by fossil fuel emissions; V increases with oil burning, Cu and Zn with coal burning, and Pb with both coal burning and auto exhaust (Charles and Norton 1986). Baron, et al. (1986) studied depositional trends of these trace metals in cores from four lakes in the Rocky Mountain National Park, CO. Only Pb concentrations changed, once apparently associated with 19th century Pb mining in Colorado, and a second time due to the recent automobile emissions. There were no historical pH changes based upon diatom stratigraphy in the four study lakes. The lack of diatom-inferred pH changes and the lack of near surface increases in Cu, Zn, and V indicated to Baron, et al. that coal and oil combustion are not yet serious sources of air pollution in the park.

Johnson, et al. (1986) studied the vertical core profiles of ten metals, Al, Fe, Mn, Cu, Ni, Zn, Pb, Cd, Cr, and Hg, as well as ^{210}Pb , to five small Precambrian Shield lakes near Sault Ste. Marie, Ontario. Pb, Hg, Zn and Cd showed marked sedimentary increases due to anthropogenic inputs. Pb averaged 18 times the background loading with precipitation loading several times greater than the background loading. The increased loading of Zn was also probably mainly due to atmospheric deposition in these lakes, but the amount was smaller than the background loading and part of it was non-anthropogenic. Johnson (1987) repeated part of this study across 14 lakes covering a broader geographical area with more variation as to human inputs. The amount of anthropogenic Pb averaged 17 times the background loadings for all lakes, and the majority of lakes had human-caused increases in Zn, Cd, Hg, and As, though at only 1.8-2.6 times the background. Sedimentary increases of Zn, Cd, As, and Pb were greater closer to industrial regions.

Sediment cores from 30 low alkalinity PIRLA (Paleoecological Investigation of Recent Lake Acidification) lakes in the northern Great Lakes states, New York, New England and Florida were examined by Norton, et al. (1992) for vertical changes in total trace metal concentrations. The eight, non-conservative-cationic, trace metals studied were Al, Ti, Fe, Mn, Pb, Zn, Cu, and V. The

cores were dated using ^{210}Pb . The mean sedimentation rate for these lakes varied between 1.26 and 1.93 $\text{mm}\cdot\text{yr}^{-1}$; the maximum for any single core was 3.40 $\text{mm}\cdot\text{yr}^{-1}$. The productivity of most of the lakes increased by 1850. Where acid precipitation was a problem, the amount of Mn in superficial sediments decreased, otherwise it was controlled by diagenetic processes in these lakes. Pb, Zn, Cu, and V were all dominated by atmospheric inputs. All of the cores showed large increases in Pb concentration prior to the late 19th century. Both Zn and Cu concentrations increased in most of the cores after 1900. Copper increases were easy to detect due to its low background and the sharp increase in its use in the last 20 to 30 years. The increases in sedimentary V concentrations, due mainly to oil burning, did not begin before 1920 and have steadily grown up to the present time. Striking increases in this metal begin a few years after the conclusion of the Second World War in almost all lakes, though these increases began as early as the 1930s in some NY lakes. The V increases were typically 0.1 times that of Pb. The dated increases in these four metals are closely linked to changes in industrial activities and increases in commercial development and transport, primarily combustion of leaded gasoline. Vertical profiles of Zn and Cu are more variable than that of V and “reveal a more complex history, possibly including the effects of sediment diagenesis and acidification of the lakes (p. 208).” The impact of acidification upon the vertical profile of sedimentary Zn is stronger than for either Cu or V. “Sediment accumulation rate for lakes from NGLS, NY, and NE are directly proportional to the inventory of atmospheric stable Pb and V, maximum accumulation rates for stable Pb, and the integrated unsupported ^{210}Pb . These relationships suggest that sediment focusing controls the accumulation rates of chemically immobile atmospheric pollutants (p. 211-212).”

White and Gubala (1990) applied sequential fractionation of sediments to an analysis of Al, Fe, Mn, Pb, and Zn deposition in three Adirondack lakes which have been impacted by atmospheric pollution. Non-residual Al showed a clear increase after 1940-1950, which correlated with increased lake acidification as inferred from enumerated diatom assemblages. The pattern of the atmospheric deposition of Zn was inconsistent, possibly due to acid dissolution of the particles where it was found. White and Driscoll (1987b) earlier noted that Mn in the water column of acidic lakes behaves like a conservative cation;

consequently its sedimentary geochemistry is shifted towards dissolution in superficial sediment layers, so sequential fractionation in acidified lakes is not useful for sedimentary analysis of this metal (White and Gubala 1990).

5. Previous Water Column and Sedimentary Chemistry Studies in Oregon and Adjacent Areas

There have been few trace metal studies of Pacific Northwest lakes. Only six relevant articles or reports from five investigations over the last 20 years were found for this review. Rabe and Bauer (1977) reported mean total sedimentary values from the non-contaminated Bell's Lake in the Couer d'Alene River Valley, ID. The total Fe concentration averaged 2.2%, Zn was 87.3 ppm, and Cu was 7.0 ppm. Dunnette (1983) published a review of trace metal data collected from mainstem streams and rivers in Oregon, including Willamette River sediment data for Zn and Cu. Dunnette's data, however, were all strictly "total recoverable", i.e., the quantity which can be obtained after heating a sample which has been acidified with HCl.. Total sedimentary Zn in the Willamette averaged 249 ppm while Cu had a mean of 42 ppm. More useful work, in terms of this research, were the report and article by Landers, et al. (1987a, b) and Eilers, et al. (1988), an article by Martin and Rice (1981), and an unpublished data set of R.W. Collier.

Landers, et al. (1987a) reported on the U.S. EPA western regional study of alpine lake water chemistry, including filterable iron and manganese concentrations from a number of Oregon and Washington lakes (none in common with this study); Eilers, et al.'s article (1988) was a summary of this report. The median filterable Fe and Mn concentrations were 15.7 and 2.5 $\mu\text{g}\cdot\text{l}^{-1}$, respectively, (Eilers, et al. 1988) for 117 lakes sampled in the Washington, and 42 in the Oregon, Cascades. Iron concentrations averaged 9.7 $\mu\text{g}\cdot\text{l}^{-1}$ in the Northern Rockies subregion, which included ten lakes in the Blue Mountains; Mn concentrations from the lakes of this subregion averaged below the detection limit for direct AAS analysis of water samples (U.S. EPA. 1979). The averages for the ten Blue Mountain lakes were $18.8\pm14.1 \mu\text{g Fe}\cdot\text{l}^{-1}$ and $4.9\pm6.5 \mu\text{g Mn}\cdot\text{l}^{-1}$ with ranges of $0\text{-}47 \mu\text{g Fe}\cdot\text{l}^{-1}$ and $0\text{-}17.5 \mu\text{g Mn}\cdot\text{l}^{-1}$ (Landers, et al. 1987b).

Collier (personal communication) collected epilimnetic water samples from 11 Oregon lakes and analyzed these samples for the filterable concentrations

of nine trace metals including six metals from nine of the lakes studied in this research. To my knowledge, this data set has never been published. The six metals in common between the two efforts were Fe, Mn, Cu, Ni, Mo, and V, and the nine lakes which both studied were Eel, Woahink, Loon, Big, Blue, Suttle, East, Paulina and Crater. His Mo data from these lakes has been included in this dissertation. Results for the other five metals can be summarized as follows. Filterable Fe concentrations in these lakes varied from 6.3 in Big, 6.5 in Crater, and 13.7 nmol·l⁻¹ in Blue to 515 in Eel and 3755 nmol·l⁻¹ in Loon (Suttle, just downstream from Blue was twice as high of Blue, 27 nmol·l⁻¹). The geometric mean for filterable Fe from these lakes was 66 nmol·l⁻¹, but there were no lakes with a concentration similar to this mean. The three coastal lakes, and a fourth one, Siltcoos sampled, but not analyzed here, had filterable Fe concentrations > 100 nmol·l⁻¹ while of the seven Cascades and East Transition lakes that Collier sampled, only one, Paulina (at 255.5 nmol·l⁻¹), had a filterable Fe concentration above 30 nmol·l⁻¹. Filterable Mn was less variable than Fe with the lowest values in Blue and Suttle Lakes (2.3 and 2.7 nmol·l⁻¹, respectively) to 65.9 nmol·l⁻¹ in East and 31.4 nmol·l⁻¹ in Paulina. None of the other seven lakes that Collier analyzed had Mn concentrations of greater than 14 nmol·l⁻¹. Filterable Cu varied even less than Mn with a range from 1.25 to 6.5 nmol·l⁻¹; the mean was 4.2 nmol·l⁻¹. Filterable V, with some exceptions, tended to have an inverse pattern to Fe in the lakes measured. Vanadium was highest in Blue, Suttle and Crater (108.5, 84, and 42.4 nmol·l⁻¹, respectively) and low in Woahink, Eel, and Loon (0.7, 3.3 and 3.7 nmol·l⁻¹, respectively). The largest differences were found in Big where the lowest value of all 11 lakes was found (0.5 nmol·l⁻¹) and Paulina, which possessed an intermediate concentration (29.4 nmol·l⁻¹). Filterable Ni was highest in Paulina and Suttle (19.5 and 19.0 nmol·l⁻¹, respectively), and lowest in East and Big (0.6 and 1.2 nmol·l⁻¹); most of the lakes had less than 5 nmol·l⁻¹ (Woahink, at 9.5 nmol·l⁻¹, was the only other lake with a concentration above 5 nmol·l⁻¹).

Martin and Rice (1981) published the only study on trace metals from sediments of an Oregon lake, Upper Klamath. They analyzed total sedimentary concentrations of seven metals, including Fe, Mn, Zn, and Cu, from the top 30 cm. Sedimentary moisture content, trace metal concentrations and ²¹⁰Pb and ¹⁴C dated sedimentation rates all point to a very rapid recent rate of

deposition of biogenic material in this lake. The moisture content of the eight cores that they collected varied from 85-92% just below the sediment-water interface to 81-88% at about 60 cm, relatively high percentages. The sedimentation rate is currently about $3.0 \text{ mm}\cdot\text{yr}^{-1}$ as measured by ^{210}Pb ; in the past century it was about $1.8\text{-}1.9 \text{ mm}\cdot\text{yr}^{-1}$ and, using ^{14}C dating, it took 3000 years to add 15 cm in the 60-90 cm zone (a calculated rate of sedimentation of $0.05 \text{ mm}\cdot\text{yr}^{-1}$). The current rate of sedimentation is very high from both a historical and paleolimnological perspective and in comparison to other lakes from the literature (e.g., Davis, et al. 1985; Håkanson and Jansson 1983). The mean total Fe concentration was 0.99%, the mean Mn value was 36.4 ppm, sedimentary Zn averaged 17.3 ppm, and Cu was 11.8 ppm. Martin and Rice noted that these concentrations were low compared to many other lakes.

The only vertical differences observed by Martin and Rice (1981) were surface enrichments by lead and manganese. The Pb increase was attributed to increased human activity in the past century. Martin and Rice believe it was apparently added through atmospheric fallout, then partially mixed down into the sediments by bioturbation. The surface increase of Mn was caused by migration of soluble Mn^{+2} from lower anoxic layers into the oxic zone followed by re-precipitation of a Mn oxide in the surface layer.

6. Selected Previous Freshwater Phytoplankton Investigations in Oregon

There have been relatively few phytoplankton studies from Oregon lakes published in refereed journals. Most of the available material is found in technical reports and graduate theses, and has been mostly descriptive in nature. Larson and Donaldson (1971) summarized the earlier literature, while Johnson, et al. (1985) covered most of the literature published between 1970 and 1984. The two largest sources of comparative phytoplankton information were Johnson, et al. (1985) and Sweet (1986, 1990). Most of the phytoplankton data used in this dissertation came from these two sources along with data from graduate theses by Mulvey (1986) on Blue Lake and Larson (1970) on Crater and Woahink Lakes as well as papers by Larson and Geiger (1981) and Debacon and McIntire (1991) on Crater. Sweet's (1986) report to the U.S. Forest Service on the predominant phytoplankton species found in Oregon and Idaho

lakes, as well as the set of reports that he made to the Oregon DEQ (Sweet 1990), have been particularly useful.

Analysis of phytoplankton species composition beyond basic abundance descriptions has been entirely absent except for those of Debacon and McIntire (1991) and Larson (1984) on Crater Lake. The scattered, relatively unanalyzed, and fragmented nature of the available phytoplankton data precludes any detailed description of the distribution of these organisms in Oregon lakes much past the brief trophic status descriptions given in Johnson, et al. (1985). Most of the phytoplankton populations found in the 19 previously-described lakes of this study (neither Clear nor Carter had their phytoplankton populations analyzed before this research) were typical for the trophic status of the lake (Johnson, et al. 1985, Sweet 1986, 1990). Oswego Lake possessed the most distinctly variant summer assemblage, probably due to the copper sulfate additions (Johnson, et al. 1985), although some of the more unusual species which occurred in Oswego were also found in the non-Cu-treated Clear Lake during this research while Lake of the Woods has a large number of peculiar species as well (Sweet 1994 personal communication).

Important Oregon indicator species of phytoplankton include the diatoms *Asterionella formosa*, *Cyclotella stelligera*, *Fragilaria crotonensis*, *Melosira granulata*, the incorrectly-identified *Stephanodiscus astraea* (Håkansson and Locker 1981; Round 1981), and *Tabellaria* spp. (Johnson, et al. 1985). Important green algae are *Ankistrodesmus falcatus*, *Oocystis pusilla*, and *Sphaerocystis schröteri*, while common chrysophytes include *Chromulina* spp. and *Dinobryon* spp. The cyanophytes *Anabaena* spp. and *Aphanizomenon flos-aquae* and the cryptophytes *Cryptomonas erosa* and *Rhodomonas minuta* are also ecologically important (Johnson, et al. 1985). Although pyrrrophytes, i.e., dinoflagellates, are seasonally important in Crater Lake (Debacon and McIntire 1991) and in many Midwestern lakes, they are not abundant in most Oregon lakes (Johnson, et al. 1985). All of the diatoms, except *Cyclotella stelligera* and *Tabellaria* spp., indicate mesotrophic to eutrophic conditions, and *Melosira granulata*, like other members of its genus (Reynolds 1984), is indicative of high turbulence. Both of the common Oregon planktonic cyanophytes favor eutrophic waters while the three green algae, two chrysophytes and two cryptophytes prefer either oligotrophic conditions or are indifferent to the trophic

status of these lakes (*Ankistrodesmus falcatus*, *Cryptomonas erosa*, and *Rhodomonas minuta*). The green alga, *Coelastrum microporum*, the most abundant alga found in Oswego Lake, occurred nowhere else among the 202 lakes reported in Johnson, et al. (1985).

Crater Lake is the only lake studied in Oregon to have a vertically stratified phytoplankton community (Debacon and McIntire 1991; Larson and Geiger 1981). The otherwise uncommonly occurring diatom, *Nitzschia gracilis*, is predominant in the surface waters of Crater Lake, while a filamentous algae, variously identified as either *Tribonema* or *Mougeotia* spp., is common at the "mid-water" depths below 80 m. Vertical stratification typically develops during the mid to late summer and lasts until late fall (Debacon and McIntire 1991). It is mainly caused by the deep light penetration found in this lake (Secchi Disc depth = between 20 and 30 m). Both D. Larson (1984, 1986 personal communication) and G. Larson (1993 presentation at the North American Lake Management Society meeting, Seattle WA) have reported changes in the Secchi Disc depth over time with D. Larson suggesting that it was due to an increase in *N. gracilis* numbers caused by increased nitrogen inputs from the National Park's sewage facilities while G. Larson believes that it is due mostly to long-term (i.e., greater than annual) climatic cycles.

Several of Oregon's lakes show signs of increased cultural eutrophication. Besides Oswego and Upper Klamath Lakes (Johnson, et al. 1985), lakes with known inputs include Devils, Woahink, Mercer and Garrison (Daggett 1994, D. Larson 1991 OLA presentation, Raymond 1991 OLA presentation, Schaedel 1991, 1992 OLA presentations). A large part of the Oswego eutrophication problem is due to drainage from the Tualatin River basin (Vaga 1992 personal communication); this was confirmed during the recent summer that the hydroelectric dam at the end of Oswego was shut down for lack of parts. During that period the lake was the clearest that both Sweet and Geiger could remember (personal communications). While cultural eutrophication is becoming a serious problem in some lowland and coastal lakes of Oregon and may be beginning to affect certain popular High Cascade lakes such as Diamond, Lake of the Woods, and Suttle, signs of two other serious anthropogenic afflictions, industrial pollution and acid rain, are not found in any Oregon lakes. Both mercury and arsenic pollution have been found, or are suspected in Dorena and Cottage

Grove Reservoirs (Dunnette 1983, Johnson, et al. 1985); however, natural causes are believed responsible, and the phytoplankton populations present in these reservoirs show no obvious signs of change. The lack of acid rain impacts on Oregon lakes is even clearer. There are a number of characteristic diatom and chrysophytan species found in the water column and on various submerged surfaces of acidified lakes (Schindler, et al. 1985, Dixit, et al. 1990); the diatom *Asterionella ralfsii* is a particularly good example of such species. None of the acid indicating species have been found in any Oregon lake so far, nor has the pH of any tested lake been below 5.5 (Johnson, et al. 1985).

7. Some Environmental Factors Controlling the Distribution of Biological Assemblages

A conceptual dispute has long raged among plant ecologists as to whether or not ecological communities really exist. A complete discussion of the argument is beyond the scope of this review. Suffice it to say, that one school, typified by the ideas presented in Whittaker's work (1956, 1967, 1978a), maintains that plant species independently respond to changes in environmental gradients, hence lack common limits to their distribution. Thus, according to Whittaker and others in this school, there is no such thing as a community, let alone a biome. (The preceding is, of course, an oversimplification of their ideas.) On the other side, a number of scientists, such as the early European plant ecologists and Shefford (1963) have long argued for the existence of plant communities while accepting that there are zones between the different communities, called ecotones, where many different species reach their limits of growth at different places during the transition between neighboring communities.

Although the ideas of Whittaker, et al. are factually correct, they seem counterintuitive to accept, particularly if an observer travels, for example, from Newport on the Oregon coast to Burns in the middle of the High Desert. A number of psychological studies have demonstrated that the human mind, in its need to organize impressions received through its senses, will impose an order on observations where none exists. Whether biomes, ecoregions, and communities truly exist or are a product of human needs is, at one level, a philosophical question of perception. However, on another level, Pielou (1975) approached the entire issue with a mathematical analysis involving the idea of

“graininess”, and essentially concluded that it was mainly a matter of the scale at which biological distributions were studied. Furthermore, in strictly pragmatic terms of whether or not such concepts are scientifically productive, i.e., do such ideas yield new understandings, both biomes and ecoregions, as well as, under some circumstances, communities or ecosystems, provide insights into ecological functions not otherwise available. That is to say, ecological identities above the population level are fuzzy-edged phenomena both conceptually and physically but which have pragmatic utility. However, having stated a few serious, and probably quite valid, reservations to the concepts of biomes, ecoregions, and communities, I now intend to use the first two as if they are completely real for the remainder of this dissertation to search for and explain patterns in the data.

Climate and physiography are two of the major factors controlling the large scale distribution of plants and animals. Since climate, geology, and the physical form of the land exist in broad-brush patterns, it is not surprising that biomes and ecoregions exist as well as broadly grade into one another. These three parameters comprise the basic physical, or abiotic, environment for organisms. Since the physical environment imposes limits on the organisms present, the result is that plant communities, biomes, and the multiply-related biological communities known as ecoregions can easily be described, even if they typically grade into one another. Consequently, changes in the physical environment appear to produce changes such as those observed in the preceding example. On the next level below climate and geology, the chemistry of an area's soils, which are derived from the previous factors, also influence the original vegetation present as well as the native animals found there and the chemistry of any water bodies in the area (Omernik and Gallant 1986).

There exist seven major non-mountainous climatic regions in North America above the Isthmus of Tehuantepec (generally regarded by biogeographers, e.g., Darlington (1957), as the boundary between the Nearctic and Neotropics). These are the Arctic, Cold Continental, Moist Continental, Steppe, Desert, Mediterranean, and Maritime. The predominant vegetation in these seven regions are tundra, coniferous forest or taiga, deciduous forest, grassland, desert shrub, chaparral, and (unique to North America) warm-weather coniferous forest biomes, respectively. Within these seven major North American biomes,

Omernik (1987) has described over 50 terrestrial ecoregions, eight of which are found in Oregon (Omernik and Gallant 1986), by combining climate with physiography, soils, and natural vegetation.

Omernik's ecoregions are only the latest manifestation of an idea that there exists an intermediate level between communities and biomes (Omernik 1987). A more important question is how useful is his version. Whittier, et al. (1988) examined the robustness of Omernik's classification by performing multivariate analyses of biotic assemblages and physical and chemical parameters in small Oregon streams found in his eight ecoregions. (A more specific description of each of Omernik and Gallant's ecoregions represented in this research effort is presented in Section I.C.) The three non-montane ecoregions (Willamette Valley, Columbia Basin, and High Desert) were clearly separable in terms of fish, macro-invertebrates, and water quality from each other and from the five montane ecoregions (Cascades, Eastern Transition, Coast Range, Blue Mountains, and Sierra Nevadas). The periphyton and physical habitat parameters had different patterns of separation. For the periphyton, the different groups were I. the Willamette Valley, II. the Cascades, Eastern Transition, and Sierra Nevadas, and III. the remaining four ecoregions. The physical habitat parameters were distinct for the Willamette Valley, the High Desert, and the Eastern Transition, with the Cascades, Blue Mountains, and Coast Range lumped together and the Columbia Basin overlapping parts of the first three ecoregions. Whittier, et al. concluded from their analysis of Omernik's approach "that Omernik's (1987) map of ecoregions of the conterminous United States can serve as a geographical framework for classifying streams (p. 1277)." They recommended Omernik's ecoregions over the more traditional river basin approach "for stratifying natural variability (p. 1277)."

Such an approach could be an important assist to the classification of biological assemblages in lakes as well. Two recent studies of lake phytoplankton assemblages, performed without using Omernik's system, suggest ecoregions may be a significant intermediate level of classification between ecosystems and biomes. Earle, et al. (1987) studied the phytoplankton from 97 lakes on Newfoundland. Using complete-linkage cluster and factor analyses, they found that seven derived environmental factors correlated with species abundances and distributions and that the species present formed 12 distinct clusters, or

possibly true species assemblages. The environmental factors were dystrophy, hardness, salinity, lake size, season, watershed influence, and P enrichment. The first three factors had a clear geographical component to their distribution with high salinity assemblages near the coastline, the hard water species along the west coast and north peninsula, and assemblages favoring dystrophic lakes limited to the interior of the island. It is important to note here that Omernik (1987, 1993 NALMS poster) also suggested that New England is, and Newfoundland may be as well, divided into core and non-core areas, and that the non-core regions could be further divisible as Earle, et al. suggested when comparing their Newfoundland lakes to lakes in Labrador.

The second important study, by Anderson, et al. (1993), examined the relationship between diatoms in lake sediments with a number of environmental parameters. Through the use of principal component analysis, they found that 72.8% of the diatom variability could be explained by the first five axes, the first three of which possess an ecoregion component to them. The first axis is largely a water chemistry one which reflects geological and edaphic conditions, primary factors in Omernik's classification. The second axis is based upon altitude and marine influence, while the third axis reflects a particular geological subunit in New Hampshire. The remaining two axes (explaining 20.0% of the variation) are related to trophic status and lake size. Omernik (1993 NALMS poster) is currently expanding his second order classification to the same lakes as Anderson, et al. described, and a synthesis of the work by both groups is anticipated.

8. The Paradox of the Plankton, A *Reprise*

The ultimate theoretical basis for this research is based upon an approach derived from a possibility first suggested in Hutchinson (1961). This section is a brief overview of the issues raised by Hutchinson and others. While this dissertation does not go deeply into this subject, the following section provides a necessary context for several observations made in the Discussion.

In December 1960 G.E. Hutchinson raised an interesting and important question for planktologists at the annual meeting of the American Society of Naturalists (Hutchinson 1961). "How is it possible for a number of (phytoplankton) species to coexist in a relatively isotrophic or unstructured

environment all competing for the same sorts of materials? The problem is particularly acute because there is adequate evidence from enrichment experiments that natural waters, at least in the summer, present an environment of striking nutrient deficiency, so that competition is likely to be extremely severe (p. 137)."

This was not a trivial question, as by Hardin's principle of competitive exclusion and as demonstrated by Gauss, there should be only a single species of algae which occupies the niche of planktonic primary producer in the apparently homogeneous environment of the summer epilimnion of lakes as these organisms are all competing for light and the same nutrients. Yet the diatom flora of Lake Michigan alone is comprised of over 700 species (Stoermer and Yang 1969), and phytoplankton samples even from small lakes typically yield between 20 and 100 species per ml of lake water. (Note: where a particular article in this section is not referenced, the citation has been given in the primary paper being discussed.)

There are certain questions which, in retrospect, have proven to have been extremely fruitful ones to ask. Hutchinson's question was a member of this category. Its result has been to stimulate literally hundreds of limnologists for the past 35 years to productively investigate the functionality of niches in freshwater ecosystems.

The initial response to this paradox was, at the time of Hutchinson's presentation, as he himself suggested, to claim that equilibrium is never obtained in natural environments. Hutchinson observed that three classes of organisms theoretically exist in respect to equilibrium, depending upon their reproduction rate when compared to the rate at which an environmental equilibrium is attained: fast, intermediate, or slow. He noted that the first and third classes should "compete under conditions in which an approach to equilibrium is possible; organisms of intermediate rates of reproduction may not do so (p. 138)." Plankton are members of the intermediate class according to Hutchinson, thus the phytoplankton species richness present may be due to a disequilibrium.

However, this was not the only possible explanation for the species richness of the phytoplankton. MacArthur's theoretical analyses of niche diversity yielded three different species abundance distribution patterns, only one of which is found in nature, the only one which implied competitive exclusion.

Hutchinson, though, observed a fourth form which was skewed towards the common species being more common and the rare species being scarcer than MacArthur's type I distribution. Plankton species fit the type IV species abundance distribution pattern. Hutchinson felt that "either non-equilibrium in time or unexpected diversity in space are likely to underlie this type of distribution (p. 140)." Unfortunately, he concluded that "(i)t is hard to believe that in turbulent open water many physical opportunities for niche diversification exist (p. 141)."

The next possible explanation that Hutchinson raised to resolve the paradox of the plankton was to suggest that some of the different species might have different micronutrient requirements such as a need for vitamins which others excreted, thus forming a sort of commensalism. In support of this idea, he noted "that many of the vitamin-requiring algae are small and ... tend to be motile. The motility would give such organisms an advantage in meeting rare nutrient molecules, inorganic or organic (p. 141)."

Another possibility that he raised in his paper, developed through conversations with Robert MacArthur, is that co-existence of two or more species may occur due to selective and/or differential predation. However, at the time of his paper, there was no evidence for this phenomenon in the plankton.

These thoughts and observations lead Hutchinson to make the following assessment. "The possibility of synergistic phenomena on the one hand and of specific predation on the other would probably permit the development of a somewhat diversified equilibrium plankton even in an environment that was essentially boundaryless and isotrophic. It may, however, be doubted that such phenomena would ever permit assemblages of the order of magnitude of tens of species to co-occur. At least in homogeneous water in the open ocean there would seem to be no other alternative to a non-equilibrium, or as MacArthur ... would term it, an opportunistic community.

"The great difficulty inherent in the opportunistic hypothesis is that since, if many species are present in a really variable environment which is controlling their competition, chance extinction is likely to be an important aspect of the process. That this is not an important aspect of the problem ... is shown by the continued presence of certain dominant species of planktonic diatoms as micro-fossils in sediments laid down under fairly uniform conditions over

periods of centuries or millennia. ... It is always possible to suppose that the persistent species were continually reintroduced from outside whenever they became extinct locally, but this does not seem a reasonable explanation of the observed regularity (p. 141-142)."

Hutchinson's final suggestion to resolve the paradox was to ask whether or not the concept of phytoplankton was valid since numerous benthic microalgae annually move into the plankton. However, he admitted that this would still leave the problem of phytoplankton diversity in the ocean. But, as he concluded, there was no correlation in the available data in a given lake district between lake area and the number of phytoplankton species, although there had not been any test of an alternative possibility that phytoplankton species richness might correlate with the length of the lake littoral instead of lake area.

I have never read nor heard of the last hypothesis being tested in the 34 years since Hutchinson's paper, so his final suggestion to resolve the paradox in lakes still remains a possibility. However its apparent inability to address the environmental causes for marine phytoplankton diversity has probably made limnologists disinterested in testing whether or not it could be valid in lakes. Nonetheless, a zooplanktologist has recently examined the role of area in predicting planktonic crustacean species richness in lakes (Dodson 1992), and found a good fit, distinct from the role of primary productivity or distance from another lake. Since this is an equivalent idea just one or two trophic levels removed from the phytoplankton, a test of Hutchinson's last hypothesis might also be informative, if it hasn't already been done.

Richerson, et al. (1970) published the first successful study to clarify how the paradox of the plankton might be resolved. They essentially suggested that physical patchiness within a lake mixed slowly relative to algal reproductive rates enabling high species diversity within a lake. "At any one time, many patches of water exist in which one species is at a competitive advantage relative to the others. these water masses are stable enough to permit a considerable degree of patchiness to occur in phytoplankton, but are obliterated frequently enough to prevent the exclusive occupation of each niche by a single species. ... This hypothesis differs from Hutchinson's by stressing the contemporaneous, rather than temporal, heterogeneity of the plankton habitat (p. 1710, 1714)."

One very important observation that Richerson, et al. explicitly made was that “(t)he various hypotheses are not mutually exclusive and any one can help (emphasis added) to explain “the paradox of the plankton” (p. 1711) ... It must be stressed that the two nonequilibrium hypotheses are not contradictory, but rather reinforce one another (p. 1714).” Richerson, et al.’s key contribution besides this explicit statement was to demonstrate that lakes are actually more physically structured than Hutchinson had originally stated. They also suggested, but did not verify, that phytoplankton species diversity might be top-down, i.e., predation, driven in part.

Petersen (1975) questioned the need for a non-equilibrium explanation of the paradox of the plankton. He proposed a theoretical model where “several species of phytoplankton can coexist in a true competitive equilibrium if they are collectively restricted from further growth by an array of different nutrients. The hypothesis requires that several nutrients be in relatively short supply and that the growth of each species be restricted by a single nutrient or a unique combination of several nutrients (i.e. a nutrient ratio). For each species to be limited by a different or a unique combination of nutrients, it is necessary that the different species possess unequal abilities in the uptake of the various nutrients (p. 35).” Petersen then reported the results of computer model simulations for the two species and the three species cases. These results mathematically demonstrated that two and three species could coexist in an equilibrium. He also performed a number of modifications to the model “including the possibility of the growth of each species being affected by several nutrients simultaneously, differences among the species in maximum growth rates and death rates, and the effects of the continual advection of fresh nutrient to the system coupled with the loss of dead phytoplankton from the system without remineralization (as, for example, by sinking). With the exception of differences in death rates, none of the modifications significantly altered the ... results (p. 42).” Both death and high sinking rates changed the equilibrium requirements to a large degree.

There are several natural examples which support Petersen’s model. First, Hutchinson (1967), as well as Debacon and McIntire (1991) and Reynolds (1984) have noted that phytoplankton occur in distinct species assemblages due to the prevailing chemical and physical conditions. Second, more nutrients

are in short supply in oligotrophic lakes than in eutrophic lakes and, as Margalef has pointed out, phytoplankton species richness is greater in oligotrophic lakes than in eutrophic lakes, which would be the logical outcome if this model is an accurate depiction of the real world. This observation is supported by nutrient addition experiments. Third, subsequent to Petersen's paper, a number of pairs of phytoplankton species from the same genus have been demonstrated to have different rates of nutrient uptake (e.g. Brand, et al. 1983).

Petersen's model suggests that "a stable equilibrium of upwards of 30 species is possible (p. 47)" due to nutrient limitations alone in oligotrophic waters.

David Tilman (1976, 1977, 1982, Tilman and Kilham 1976) expanded and partly verified Petersen's model for freshwater phytoplankton. Tilman's expanded theory basically suggests that species in homogeneous environments partition resources, i.e., specialize in their requirements for available nutrients, light, etc., and through nutrient competition, actually increase the diversity of natural assemblages. Tilman (1982) presented an extensive and exhaustively detailed explanation of the theory with numerous examples far beyond the scope of this review. Two interesting features stand out however. Tilman deliberately used a graphical approach to represent resource-dependent growth isoclines, with the consequence that the area of a species's niche, as least in two dimensions, can be clearly defined at the Zero Net Growth Isocline, or ZNGI. The graphically-depicted ZNGI then can be used to make testable predictions.

The second interesting feature of Tilman's resource partitioning extension was a series of predictions with evolutionary significance. First, selection for optimal foraging (for resources) acting upon co-occurring individuals of each species produces the stable coexistence of various pairs of competing species only as an incidental effect. Second, the types of resources which are being competed for should not cause major, qualitative, differences in ecological patterns as distinct from the result of individual pairs of species in competition, i.e., the scale of competition does not drive ecosystem structure or productivity, only its diversity. Third, according to Tilman's theory, the "superspecies" which outcompetes every other species for a particular resource will relatively quickly splinter into multiple species which are specialized in better utilizing particular assets in a spatially heterogeneous environment. This results in a

multi-species-complex derived from the ancestral superspecies. Such complexes are frequently observed in the natural world among plants (Tilman 1992, p. 255), among diatoms, particularly the *Fragilariaceae* (p. 256) along with the *Thalassiosiraceae* (Håkansson and Locker 1981, Håkansson and Kling 1989, 1990, Theriot, Stoermer and Håkansson 1987), and probably in other divisions of algae as well. Fourth, the species richness of plants and other primary producers should reach a maximum in moderately resource-poor habitats (just as Petersen (1975) predicted for lake algae). Finally, the species composition of a plant community, or of other assemblages of primary producers, should be determined by the ratios of the supply rates of limiting resources, not absolute concentrations, as Petersen suggested earlier.

Ulrich Sommer has spent a considerable amount of time testing the resource-ratio hypothesis on freshwater phytoplankton. Initially using a chemostat (Sommer 1983), he found that the relative abundance within a multi-species community could be controlled by varying the ratio of the limiting nutrients. Next (Sommer 1984), by using pulsed additions of phosphorus, he found that a large amount of the natural diversity in a system could be maintained without invoking the idea that different species could be limited by different nutrients, and concluded "(a)lthough interesting from a theoretical point of view, limitation of different nutrients (can) explain only a small proportion of the diversity and species richness of natural phytoplankton, even if allowance is made for the usually neglected trace elements (p. 633)." Based upon this, his assessment was that oscillating nutrient equilibria was the best explanation for the observed species richness of natural assemblages of phytoplankton. He followed this up with another paper (Sommer 1985) reporting similar results using two limiting nutrients (phosphorus and silicon). He explained the results from both papers as selecting for three different kinds of specialists, velocity-adapted, affinity-adapted, and storage-adapted with the restriction that silicon could not be stored. He concluded with the following observation, "Since Si is probably lost more by sedimentation than it is recycled by grazing, high supply rates cannot be maintained in a stratified system without significant external supply. As a consequence, the diatom bloom is transient and reflects past conditions rather than the actual nutrient status. Conversely, continuous culture experiments (both steady state and

pulsed state) erase “history”. They certainly give information about the competitive ability of species, but a straightforward prediction of biomass proportions in a lake from resource ratios without consideration of time lags is possible only in exceptional cases (p. 345).”

Despite his criticisms of Tilman’s approach, he and S. Kilham joined to write a critical assessment of work by Smith and Kalff who concluded “that among competing phytoplankton there is no partitioning of the gradient of phosphorus availability and that competition for phosphorus occurs to the advantage of small algae (p. 436, Sommer and S. Kilham 1985).” Among other points, Sommer and Kilham asserted that the outcome of competition for phosphorus was not based upon size alone, and that Smith and Kalff’s own data suggested the possibility of resource partitioning.

Sommer next tested nutrient competition through enrichment experiments in a mesotrophic lake in northern Germany, Schöhsee (Sommer 1988). He found continuous Si limitation of the diatoms and interrupted N and P limitation and concluded that the latter conformed better to Richerson, et al.’s contemporaneous disequilibrium and to his earlier pulsed-state competition experiments.

By the conclusion of his next paper (Sommer 1989), where he reported on a series of enrichment bioassays in a hypereutrophic lake, Sommer had started to become convinced that the results of laboratory physiological studies could be successfully transferred to non-steady-state field conditions and that the resource ratio concept of Tilman’s appeared to be valid. It was also in this paper that he added an interesting twist to the developing synthesis, namely that the dependence of species composition on resource ratios applied not only to essential resources, but also to resources which could substitute partially or completely for one another. In doing so, Sommer significantly expanded upon and transformed an earlier idea of Tilman’s. I believe the most significant part of this paper was his finding that *none* of the 13 dominant species in Großer Binnensee possessed an identical response pattern to the ratios of possible limiting resources, a pair of substitutable resources, light, and to zooplankton grazing. That is to say, each species had a unique resource ratio niche.

In Sommer's most recent paper (Sommer 1993), he expanded his study to another lake and attempted an analysis which sought to include time lag responses into the competition model. Fourteen of 16 species studied showed a significant response to one or more resource ratios, and he concluded his paper with the observation that "multiple resource-ratio gradients seem to be important in nature (p. 845)." He also pointed out two difficulties, one of which is a possible contradiction with the theory. The possible contradiction was the scarcity that he found of species with intermediate resource ratio requirements. This contrasts with the concept of succession as a gradual progression along a one resource-ratio gradient, a later extension of Tilman's to the basic equilibrium theory. The other important difficulty that Sommer observed was the presence of a "false" correlation for a particular nutrient resource-ratio due to the interactions of these two nutrients with a common third factor. The concern that Sommer expressed about this phenomenon (and which I agree with) is that "(w)ithout knowledge from competition experiments (studying each particular resource ratio) it cannot be determined which resource ratio is causally relevant and which is not (p. 843)." Another recommendation that he made in this paper was the essentiality of using only relative numbers or biomass vs. ratios, not absolutes to test competition theories.

Independent of the approach discussed in the articles reviewed before, Tim Allen (Allen and Koonce 1973, Allen and Skagen 1973) analyzed weekly phytoplankton samples from Lake Wingra using Principal Component Analysis (PCA) and ordination of transformed data and found that the major taxonomic divisions formed distinct clusters, suggesting that they possess ecological integrity. Based upon his analyses, he also identified three basic stratagems for persistence in the plankton: 1) being ungrazed with a low productivity and a high standing crop, 2) being heavily grazed with a low standing crop while having a high productivity, and 3) being lightly grazing and having a high productivity, but being limited by short-term environmental conditions. The persistence for each group on an annual scale, was long, short, and intermediate, respectively. When the data were standardized to unity, a procedure which was also used to form Allen's tactical groupings, the species again clearly clustered by taxonomic division, not by productivity; Allen took this to mean that each major division has members which follow the previously stated

stratagems. He concluded "that strategic affiliations tend to define an organism's functional place in the community: for example, persistent species with slow growth rates or rarer species with very rapid growth rates. Tactical groups, however, tend to identify temporal and specific environmental optima of species (p. 1243-1244, Allen and Koonce 1973)." This synthesis meant that Allen had defined 12 distinctive niches before the subsequent resource partitioning covered above. The other unique feature of his approach was to integrate grazing with resource limitation, a feature which has not been otherwise well presented.

The combination of resource ratio partitioning, persistence stratagems and grazing tolerance, as well as the limited phenomenon of short-term non-equilibrium appears to adequately explain Hutchinson's "Paradox of the Plankton" if the number of limiting resources is greater than just light, temperature, and the three major nutrients. Therefore, widespread limitation by trace metals and vitamins needs to be thoroughly verified in order to provide a sufficient number of niches to accord for the observed species richness, hence to resolve the paradox.

C. Study Area

1. General Comments and Climate

The general area covered in this thesis is the entire state of Oregon, less the southeast quarter. Oregon is bounded on the west by the Pacific Ocean, on the north by the Columbia River and state of Washington, on the east by the state of Idaho and the Snake River, and on the south by the Klamath-Siskiyou mountains and states of California and Nevada. Its mid-latitude location causes it to have definite seasons, although these are greatly modified by westerly winds from the Pacific Ocean which moderate temperatures and bring large amounts of precipitation to the western part of the state (Dart and Johnson 1981). Several mountain ranges cross and/or are found within the state, the most important of which are the Cascades. These mountains divide the state into three unequal climatic and vegetational regions, the mild, humid, (formerly) forest-covered west, the semi-arid, grass and shrub-covered east, and the cool, mostly forested mountains themselves. The climates of these three regions are quite distinct. West of the Cascades summers are warm and

usually sunny, while winters are mild and characterized by persistent cloud cover; the annual precipitation is heavy with a winter maximum. East of the Cascades, summers are hot, winters considerably colder and clearer, the growing season much shorter, and the precipitation on the order of 20 to 40 cm annually as opposed to the 100 cm plus typical to the west (Dart and Johnson 1981). These differences are made even more pronounced by the difference in mean elevation between these regions. West of the Cascades, outside of the Coast Range and Siskiyou Mountains, elevations of less than 300 m above sea level are typical, while in Eastern Oregon, the average elevation is 900 to 1500 m. Within both the Cascades and the Blue Mountains of northeastern Oregon, elevations over 3000 m can occur, while in the Siskiyou, heights of 2000 m are not uncommon (Dart and Johnson 1981). These high elevations produce the third climatic and vegetative region of Oregon, the moist (up to 250 cm annual precipitation), cold mountains.

2. A Generalized Geological Description of the Study Area

Another important cause of variation in Oregon is its geology. Oregon has an extremely diverse geology (Alt and Hyndman 1978; Orr, et al. 1992). The Coast Range are low folding mountains formed by sedimentary rocks of a marine origin. Much of the northeastern plateau of the state as well as some of the western Cascades and deeper rocks of western Oregon valleys are basalts dating from the great Columbia River flood basalts of the Miocene (Alt and Hyndman 1978; Tarbuck and Lutgens 1984). On top of these basalts are 12 million year old andesites and rhyolites of the western Cascades, and the Recent and Pleistocene High Cascade andesite volcanoes such as Mt. Hood, Mt. Mazama, Mt. Jefferson, Belknap Crater, and the Three Sisters. The oldest superficial rocks in Oregon are those that form the Blue Mountains in northeastern Oregon and the Siskiyou in the southwest. These mountains originated about 200 million years ago, during the Triassic (Alt and Hyndman 1978). The Blue Mountains are believed to be part of a then near-coastal range of volcanic mountains, much as the Cascades are today (Alt and Hyndman 1978), while the Klamath-Siskiyou are several terranes that "docked" on the Oregon coast sometime later due to drifting of the North American plate and Pacific Ocean sea floor spreading (Orr, et al. 1992; Priest 1986 personal

communication). The largest amount of superficial metamorphic rocks in the state, including eclogite, blueschist, and garnet, are found in the latter mountains, as are much of the state's more valuable hard minerals (Priest 1986 personal communication).

The final major cause of Oregon's geological diversity was the Pleistocene glaciations and glacial lakes. The most readily apparent product of these glaciations was the formation of dozens of lakes due to glacial scouring and morainal deposition. Suttle and Wallowa Lakes are excellent examples of the results of these processes. In addition, many of Oregon's coastal lakes were formed by the rising sea level (due to the melting of the ice sheets) damming coastal streams with sand. Examples of the latter process include Woahink, Eel, and Mercer Lakes.

However, there was a larger and much more important product of the Pleistocene glaciations than the preceding lakes. Prior to the Pleistocene, the Columbia flood basalts of the Miocene had covered northeastern Oregon except the Blue Mountains, and had filled in a number of westward oriented drainages in northwest Oregon (Beeson 1986 personal communication). The Coast Range, north of the Klamath-Siskiyou, developed during the latter half of the Miocene, about 15 to 20 million years ago (Alt and Hyndman 1978). The resulting trough between the Coast Range, the Siskiyou and the early Cascades filled in with sediments, first forming a shallow bay which eventually filled to form the early Willamette Valley. During the Pleistocene, northeast of Oregon, there formed, at the end of each of the 20 or so known glacial advances, a glacial lake, Lake Missoula. This lake, though small as glacial lakes go, was remarkable in that it filled and emptied over 40 times in a period of about 1500 years just during the last glacial retreat alone (Pielou 1991). The lake was bounded by high ground to the southwest (the Bitterroot Range) and on the northeast by the Cordilleran Ice Sheet; however, at the extreme northwest corner of the lake was a relatively narrow ice dam formed by the Purcell trench lobe, separating Lake Missoula from Glacial Lake Columbia. The cycle of flooding and refilling worked as follows (from Pielou 1991): During the warming climate, the ice sheet steadily (more or less) melted, slowly filling the lake basin to a depth of several hundred meters over the course of several years. However, eventually the lake became deep enough to float the ice dam formed by

the Purcell trench lobe. Once the ice was lifted free of the lake floor, it no longer functioned as a dam, and there was a catastrophic flood as Lake Missoula's water suddenly flowed out under the ice, first into Lake Columbia and then across the east central part of Washington state. The entire lake probably drained away in less than two weeks. This glacial outburst, or *jökulhlaup*, scoured eastern Washington, forming the channeled scablands and the Grand Coulee. The floodwaters poured down the Columbia and through the Gorge; however, the waters pooled behind the Coast Range due to the constriction in the Columbia's valley north of Portland. The floodwaters then backed up, covering the Willamette Valley from Lake Oswego to Eugene up to a depth of 200 m (Priest 1986 personal communication), before emptying into the Pacific. The temporary lake thus formed is now referred to as Glacial Lake Allison (Orr, et al. 1992). In this quiet backwater, the silts and the clays eroded from the basalt beds of eastern Washington had time to settle out of the water column before the lakewaters drained into the Pacific. The consequence was the rich agricultural soils of the present Willamette Valley. Following these floods, probably during every Interglacial, the Willamette River reformed, and renewed its erosion of both the Western Cascade foothills and the Valley floor proper. However, the very even floor of the Valley formed by the settling out clays and silts produced a river that wandered greatly, like a much older stream. This resulted in numerous oxbows and, with the high beaver population that preceded the Europeans, created a very wet and lush landscape filled with lakes, ponds and marshes. Even after the European clearance of the Valley's forests and drainage of its ponds and lakes (including Lake Labish, a five meter deep lake northeast of modern Salem), a number of oxbows still survive in the northern half of the Valley, including Clear and Mission Lakes in Marion County, and the predecessor of Oswego Lake, Sucker Lake. The preceding geological events, especially the Pleistocene glaciations, and the state's generally moist climate, are the origins for most of Oregon's numerous lakes.

3. Ecoregions of Oregon

The diversity of Oregon's climatic regimes and geological origins has had a major impact upon the diversity of its ecosystems. Classification of ecosystems in the United States for management purposes has always been

challenging, and it is particularly difficult in mountainous regions (Omernik and Gallant 1986, Omernik 1987) such as occur in large areas of this state. Recently the concept of an "ecoregion," based upon a *variety* of characteristics, as opposed to the older viewpoint of using just a single one, has been developed (Omernik 1987). Omernik and Gallant (1986) published one such multiple characterization for the Pacific Northwest based upon four major characteristics: land surface form, potential natural vegetation, land use, and soils. These characteristics are essentially derived from an area's climate and geology. Omernik and Gallant identified eight major ecoregions in the state of Oregon (Figure 2). If Oregon is divided on the basis of Köppen's climatic classifications into "Maritime", "Montane", and "Steppe" climates, then two of Omernik and Gallant's ecoregions are Maritime, two are purely Montane, two are Steppe, and one each are intermediates between Maritime and Montane and Montane and Steppe. Furthermore, within each of the climatic regimes, the ecoregions can be separated on the basis of geological origin. These eight ecoregions are, respectively, the Coast Range, the Willamette Valley, the Cascades, the Blue Mountains, the Columbia Basin, the Snake River Basin/High Desert, the Klamath-Siskiyou (called the Sierra Nevada by Omernik and Gallant), and the Eastern Cascades Slopes and Foothills or Transition Zone. Six of these eight were represented by lakes sampled during this investigation. One of the missing ones, the Columbia Basin, lacks natural lakes, and the eighth, Oregon's High Desert country, while possessing playas and fault block lakes as well as numerous reservoirs, was not included in the final set of sampled lakes due to the lack of thermoclines in most of the lakes and general distance and/or difficulty in sampling.

4. Specific Lake Descriptions

The following lake descriptions have been drawn from a variety of sources. Lake areas, maximum depths, watershed areas, and origins are from Johnson, et al. (1985) and the U.S. Geological Survey (1977, 1979), geological characteristics are based upon the descriptions of Alt and Hyndman (1978), Omernik and Gallant (1986), Orr, et al. (1992), and personal communications by Beeson and G. Priest, phytoplankton species composition are from Sweet (1986 and 1991 personal communications), and watershed characteristics are from

Figure 2. Omernik and Gallant's (1986) Ecoregions of Oregon.

Key: ▲ soft, low alkalinity ● high conductivity, low alkalinity
 ■ soft, high alkalinity ⊗ hard, high alkalinity

Region I. Maritime climate A. Coastal ecoregion *
 B. Willamette Valley ecoregion

Region II. Montane climate A. Cascades ecoregion
 B. Eastern Transition ecoregion
 C. Klamath-Siskiyou ecoregion
 D. Blue Mountains ecoregion

Region III. Steppe climate A. Columbia Basin ecoregion
 B. Oregon High desert ecoregion
 C. Northern Basin and Range ecoregion

*: Ecoregions based upon Omernik and Gallant (1986)

Johnson, et al. (1985) and personal observations. Chemical characterization is derived from data in Johnson, et al. and U.S. Geological Survey reports based upon criteria discussed in the Methods and Materials section of this dissertation.

a. The Coastal Ecoregion

This region includes the Coast Range and the coastal valleys and terraces (Omernik and Gallant 1986). Most of the terrain is dominated by low mountains with typical elevations of 450 to 600 m which were formed largely from marine sedimentary rocks. Due to regular maritime low pressure systems and the moderate orographic relief, precipitation varies between 150 and 300 cm per year, with the bulk falling primarily in the winter. The annual evaporation rate is between 50 and 70 cm. The region was originally heavily forested with Douglas fir, western hemlock, Sitka spruce and western red-cedar, or arbor vitae. Understory vegetation includes madrona, wild rhododendron, willows, vine maple and red alder. Within the coastal sand dune subregion (where the majority of the region's lakes are found), beach pine (a dwarf variety of lodgepole pine) is the most important tree species while the dominant species of shrub in the sand dune community is a European invader, Scotch broom. Native coastal shrubs include Oregon grape and salal. Some Douglas firs and stunted Sitka spruces can also be found in the more protected areas. Soil sources include sandstone, siltstone, shale, basalt and sand.

The lakes in this ecoregion are all of relatively recent origin. Most of them were formed by shoreline processes since the last glacial advance. Woahink, Mercer, Siltcoos, and Eel Lakes are drowned river valleys, dammed up by sand dunes. Smith Lake (Clatsop Co.) is an interdunal lake, formed in the depression between two fossil sand dunes, while Cullaby, Clear (Lane Co.), Munsel, and Carter Lakes are lakes which have formed between sand dunes to their west and coastal bluffs created during an earlier period of higher sea level. Two of the sampled lakes in this ecoregion are reservoirs, Olalla and Valsetz, formed in 1957 and early in this century, respectively; regrettably (as it had both good salmonid runs and an interesting biology), Valsetz Lake was drained in the fall of 1988. The remaining two lakes sampled in this ecoregion, Loon and Triangle, were formed by a third major process, landslides. Loon Lake formed due to

falling sandstone blocks from the west side of its valley damming up the drainage about 1460 yrs BP as determined by ^{14}C dating (Johnson, et al. 1985). Triangle Lake was formed earlier when a tilted block of sandstone from the north side of the valley slide into Lake Creek (Johnson, et al. 1985). Recent seismic research (Priest 1989 personal communication) suggests that the Oregon-Washington region is shaken by very severe earthquakes (Richter scale of Magnitude 8 or greater) every 400-600 years. Some geologists now believe that both of the latter lakes were formed as a result of such earthquakes. No other lakes from the Coast Range ecoregion were cored in this study. Individual lake descriptions for those analyzed for trace metals follow.

Woahink Lake is located in Lane County, just south of Florence and the Siuslaw River. It is about five kilometers east of the ocean and some 500 m east of the active sand dunes of the Oregon Dunes National Recreational Area. Between the sand dunes and the lake is U.S. Highway 101. It is surrounded by hemlock-cedar-Douglas fir coniferous forest and the lakefront is lined with homes and summer cottages. The watershed is approximately 15 km² and over two-thirds of it lies northeast of the lake. The lake is about 330 ha in area and has a maximum depth of 20.7 m. In terms of general water chemistry characteristics, it is a soft water, low alkalinity, oligotrophic lake with a very high conductivity. The relatively high conductivity is a characteristic common to coastal lakes due to the high concentrations of NaCl salt crystals in the near coastal airshed. Water in this lake has a residence time of 1.2 years. The relative abundance of the spring-summer phytoplankton assemblage is 28% *Cyclotella stelligera*, a centric diatom, and 36% two non-nitrogen-fixing cyanophytes, *Anacystis marina* and *Chroococcus* sp.; the rest of the phytoplankton assemblage are mostly flagellates (primarily *Rhodomonas minuta*) greens, and other diatoms.

Due to weather conditions during three separate sampling trips to Woahink Lake, both water chemistry and sediment cores were collected from two different locations in the lake (Figure 3). Although this was a problem in terms of replicate sampling, it was also serendipitous with respect to demonstrating anthropogenic effects upon lake sediments as will be described later.

Eel Lake is an oligotrophic coastal lake in Douglas County. It is roughly 137 ha in area with a 25 km² drainage basin and a maximum depth of 19.8 m.

Excluding the absence of summer homes, it is very similar to Woahink in terms of depth, watershed vegetation, proximity to the Pacific, water chemistry, trophic condition, and human impacts. The superficial geology of both watersheds is composed sand and sandstone (Alt and Hyndman 1978). The common sandstones of Oregon are usually graywackes and arkoses, while the sands tend to be composed primarily of quartz and feldspars, producing a gray sand. The residence time for water in this lake is 0.5 years. Both Woahink and Eel Lakes are oxygenated to the bottom in the summer, although the hypolimnion of Eel Lake tends toward oxygen depletion (For example, hypolimnetic D.O. was only one-third of the epilimnetic concentration in August 1981). The phytoplankton of Eel Lake was dominated by *Cyclotella stelligera* and *Rhodomonas minuta*.

Mercer Lake is a meso- to eutrophic lake in the coastal region of Lane County north of Florence. It is a Y-shaped lake, 145 ha in area with a maximum depth of 11.6 m. Its drainage basin is 22 km² in area and was over 90% forested at the time of sampling. The western branch of the lake is lined with summer cottages and homes as is half of the northern branch. The shoreline of the eastern branch is mainly deciduous forest, although most of the forested area in the watershed has a similar species composition to those surrounding Woahink and Eel Lakes. The conifers in the northeastern part of the watershed were logged off subsequent to the second sampling of this lake; thus, the cores used in this research predate the recent very heavy siltation of Mercer Lake. Although it is a mesotrophic to eutrophic lake, Mercer is still oxygenated to the bottom. The phosphate concentration before the spring phytoplankton bloom is 30-35 $\mu\text{g}\cdot\text{l}^{-1}$ as opposed to 10-15 for Woahink and Eel Lakes. The conservative water chemistry and geology are similar to those for Woahink and Eel Lakes. The residence time for Mercer Lake is 0.3 years. The dominant spring-summer phytoplankton species are the diatoms, *Asterionella formosa* and *Fragilaria crotonensis*, the cyanophytes, *Anabaena* sp. and *Chroomonas* sp. and the flagellate, *Rhodomonas minuta*. A dominant fall species is the diatom, *Cyclotella stelligera*, while in 1974, the diatom, *Tabellaria fenestrata*, was abundant, an observation supported by sedimentary diatom counts herein.

Carter Lake is the fourth coastal lake analyzed from the Coast Range ecoregion. It is a small (12 ha), shallow (3.7 m), oligotrophic lake with a

Figure 3. Bathymetric map of Woahink Lake indicating sampling stations.

drainage basin of 3.3 km² which is about half forested with the remainder in sand dunes. The lake is located in Douglas County, just west of U.S. 101 about 13 km south of Florence. There is a small, primitive U.S. Forest Service campground on the northwest shore of the lake and a boat launch on the north part of the east side. Immediately to the west of the lake is an approximately 10-15 m high steep sand dune. The water chemistry and geology are similar to the three previous lakes. The retention time is about 0.2 years. It was sampled in August 1985 during a major drought which had reduced the water level by 2.6 m, causing the lake to be divided into northern and southern parts. Cores were taken from both basins. The phytoplankton from this lake are dominated by flagellates, particularly *Rhodomonas minuta*, and by diatoms, including two species of *Cyclotella*. None of the four lakes discussed so far is greater than 20 m above sea level, nor is any part of these lakes more than six kilometers inland from the Pacific.

Loon Lake is moderate-sized lake in the Douglas County portion of the Coast Range proper. It is 119 ha in size and has a maximum depth of 32.0 m. The watershed is 221 km², the lake lies 128 m above sea level and is about 32 kilometers inland from the Pacific Ocean. Over 95% of the watershed is forested, although there are a few summer homes along its southern (or upstream) shores. The water chemistry is low in all dissolved salts with a low alkalinity and low concentrations of phosphorus, making it usually an oligotrophic lake. However, when it was resampled in September 1989 after four summers of drought conditions, the ranger at the BLM campground on the western outlet reported observing that August the first phytoplankton bloom that he had ever seen on the lake in over seven years of working there. Three species of diatom were common in the phytoplankton, *Cyclotella stelligera* (20.5%), *Asterionella formosa* (6.6%), and *Amphora ovalis* (1.7%), as was a green alga, *Ankistrodesmus falcatus* (20.5%), and the flagellate, *Rhodomonas minuta* (12.0%). The superficial geology of the area is either sandstone or a mudstone/sandstone mix.

Triangle Lake is the remnant of a much larger lake. It is located in the Coast Range of western Lane County at an elevation of 212 m, about 44 kilometers east of the Pacific Ocean. The present lake is 29.0 m deep and 113 ha in area, while the watershed has an area of 134 km². The older lake shoreline,

which Oregon Highway 36 skirts along the northern side, is about six times as long in length and the flat lake floor, now pasture, is about the same to half again the current lake's width. This suggests that original lake had a surface area approximately eight times the present one. Despite the agricultural land upstream from the lake and summer homes around half its shoreline, the majority of the watershed (> 90%) is heavily forested. Both Loon and Triangle Lakes have watersheds dominated by Douglas fir. Their residence times are on the order of 0.2 years. The entire watershed of Triangle Lake is composed of marine sandstones. Water in the lake is soft with a low alkalinity and phosphate concentrations in it are moderate. The lake is considered to be mesotrophic (Johnson, et al. 1985). The most abundant species of phytoplankton is *Asterionella formosa* at 15.7% of the total in May 1982. Other common diatoms include *Achnanthes minutissima* (8.3%), *Synedra* spp. (13.8%), and *Tabellaria fenestrata* (2.8%) as well as five common species of flagellates including *Rhodomonas minuta* (11.1%) and the chrysophyte, *Chrysococcus rufescens* (12.0%). One interesting, but rare species of diatom, found only in Triangle Lake among the 21 studied for fractionated trace metals, is *Rhizosolenia eriensis* (2.8%).

Along with Woahink and Eel Lakes, both Munsel Lake and Olalla Reservoir were analyzed for the vertical distribution of total concentrations of trace metals using neutron activation analysis. **Olalla Reservoir** is a mesotrophic to oligotrophic body of water which is kept filled with Siletz River water rather than from drainage of its own watershed. The reservoir is 45.7 hectares in size and has a maximum depth of 19.8 m. It is at an elevation of 50 m about 10 kilometers from the Pacific Ocean. Although relatively close to the ocean, its conductivity is less than that of Loon Lake due to the source of most of its water, making it classified as a soft water, low alkalinity lake. The immediate watershed is covered with second growth Douglas fir on a siltstone and sandstone substrate. No phytoplankton data were available for this lake.

Munsel Lake is a mesotrophic to oligotrophic lake located five kms north of Florence and an equal distance in from the Pacific. It has a maximum depth of 21.6 m and an area of 44.5 ha. The northwest side of the lake was originally fronted by sand dunes and the water adjacent to them is rather shallow. The rest of the lake is next to steep hills and the depths are correspondingly

greater. The lake is 27.5 m in elevation. The total watershed is 4.4 km²; about a quarter of it is the lake itself and three-quarters of the remainder is forested by conifers. The retention time is about one year. Important species of phytoplankton include *Cyclotella stelligera* and *Rhodomonas minuta*. *Anacystis* sp., *Kephyrion* spp. and *Rhizosolenia eriensis* are also seasonally important.

b. The Willamette Valley Ecoregion

This region consists of the valley floor of the Willamette River, the middle part of the Umpqua River basin, and the area north of the Willamette-Columbia confluence up the lower Columbia to the lower Lewis River. The terrain is very flat with elevations usually between 30 and 90 m, although there are a few hills (both previous to the Columbia River basalts and due to secondary volcanic eruptions during and after the flood basalt period, i.e. Portland's Mt. Tabor and West Slope) which exceed 200 m above msl. Annual precipitation is about 100 cm, mainly during the winter, and evaporation is typically between 70 and 80 cm. The original native vegetation was mixed stands of Oregon white oak and Douglas fir on the drier ground with some big-leaf maple and some grand fir at higher elevations. Cottonwood, willows, and red alder were common riparian tree species. There were also originally extensive wetland regions with sedges as the primary form of vegetation, partly due to the general flatness of the terrain and partly due to a large beaver population, and limited patches of prairie vegetation dominated by fescue and brome grasses, particularly on the south sides of the hills, or "buttes" as the early European settlers called them. This vegetation pattern has been almost completely replaced by pasture and agricultural crops (grains, grass seed and hay, fruit trees, berries, and row vegetables). The majority of Oregon's inhabitants live here and, with one exception, all of the larger cities in the state are found in this ecoregion. Water pollution, due to the urbanization of this region, is an important local problem and some air pollution is also present. The valley soils are mainly formed from alluvial and lacustrine deposits originating from the Glacial Lake Missoula floods.

The only natural lakes remaining in this region are river oxbows, although there were originally many wetland depressions and beaver "ponds," some of which were deep and large enough to have been considered lakes by the early European explorers, trappers, and settlers. The largest of these was Lake

Labish, just northeast of Salem, currently primarily in onion fields; the second largest in area is now covered by Fern Ridge Reservoir. Lake Labish has been estimated as having a minimum surface area of more than half of Siltcoos Lake up to a suggestion that at one time it was 16 kilometers long and nearly three wide (Orr, et al. 1992). A permanent drainage system, the Labish Ditch, is required to prevent Lake Labish from refilling partly.

The eight lakes cored in this ecoregion were all either oxbows of the Willamette, Columbia, or Tualatin Rivers or man-made (three reservoirs and a gravel pit). Only two lakes from this ecoregion were analyzed for fractionated trace metals (Oswego and Clear, Marion Co.). Neither the gravel pit (Wirth Lake) nor any of the sampled reservoirs (Dorena, Cottage Grove, or Silver Creek) were analyzed. Mission Lake and Blue Lake (Multnomah Co.) were not analyzed either, Mission Lake due to its sedimentary composition (all river sand and fine gravel, as this is a very recently formed oxbow), while cores from Blue Lake are still available for analysis.

Oswego Lake is 160 ha in size and 16.8 m deep at an elevation of 30 m. Its watershed of 16 km² lies entirely within the city of Lake Oswego. Consequently, over 72% of the watershed is considered to be urban in nature. Another 12.6% is forested, mostly with Douglas fir and second growth deciduous trees such as alder. The lake has hard water with a high alkalinity. Oswego Lake was originally much shallower; its depth was increased by a small hydropower dam and a channel was cut between it and the Tualatin River early in this century. The channel was redredged shortly after World War II. Water for both maintaining its current depth and producing hydropower is taken from the Tualatin River. The lake is hypereutrophic (Johnson, et al. 1985) with a P concentration of over 125 $\mu\text{g}\cdot\text{l}^{-1}$. This concentration is due to significant amounts of nutrient input from land use activities surrounding the lake and upstream in the Tualatin River valley. Interestingly, the lake had its clearest summer recently when the hydropower turbine was broken (J. Sweet and N.S. Geiger, personal communications); hence no water was being drawn through the canal connecting the lake with the Tualatin River. The phytoplankton population is unique. "With the exception of *Rhodomonas minuta* which is widespread, the dominant algae are not found in any other lake sampled in this statewide inventory, even at low densities. It may be that the

annual additions of copper have a significant effect upon the phytoplankton species, with only copper tolerant species able to survive (Johnson, et al. 1985, p.110).” In addition to *Rhodomonas minuta*, other common species are *Coelastrum microporum*, *Pediastrum duplex*, and *Nitzschia microcephala*. Over two meters of sediment have been added to the lake floor since the hydropower dam was constructed, giving it the highest sedimentation rate of all of the lakes studied. The superficial geology of the watershed is composed largely of Columbia River basalts with some Lake Allison silts, which are eroded and chemically altered Columbia River basalts. Another important local geological phenomenon is the presence of mineable iron ore beds near the lake proper. Iron mining by the Oregon Iron and Steel Company was active from 1867 to 1894 (Orr, et al. 1992). While the mine was not a financial success, the iron beds provide a significant amount of metal inputs into the lake, especially during the summer when the hypolimnion goes anoxic. Thus, the iron bed has increased the total metal load to the lake, its sediments and plankton. Retention time is about 0.2 years when the hydropower plant is working.

Clear Lake (Marion Co.) is a small oxbow of the Willamette River just north of the Salem-Keizer area (the lake itself actually forms part of the city limits of Keizer). It is 3.5 m deep and has a surface area of 10 ha. Clear Lake is a hard water, high alkalinity lake. It is also considered to be a eutrophic lake as the summer P concentration, i.e., *after* the spring bloom, is $20 \mu\text{g}\cdot\text{l}^{-1}$, while summer Secchi disc readings are 0.7 to 0.8 m. The original watershed, except immediately adjacent to the lake where willows, a few oaks and Douglas firs grow, is entirely agricultural land with only a few farm houses and a retirement center, which provided access to the lake. While the immediate drainage area is only about 7 km^2 , both Claggett Creek and the Labish Ditch (keeping the old Lake Labish bed dry) drain into it now. The growing residential neighborhood, located just southeast of the lake and which takes its name from it, is in the Lake Labish watershed, so the surface drainage of this (at the time of sampling) small community now flows into the lake. The combined flow rate of Claggett Creek and the Labish Ditch averaged about $0.1 \text{ m}\cdot\text{sec}^{-1}$ in July 1976 (U.S.G.S. 1977). This rate means that the lake has a theoretical retention time of 0.05 years; however, Clear Lake is small and protected enough to vertically stratify in the bottom 1.5 meters; the latter fact implies a longer

residence time, given the lake's shallowness. The lake elevation is 34 m above sea level, and it was flooded by the Willamette, about 300 m away, as recently as 1985. As would be expected, the superficial geology of the watershed is composed entirely of Lake Allison silts. Three phytoplankton samples have been analyzed from this lake. In 1976 the dominant species were *Pediastrum* spp., *Fragilaria capucina* and *Melosira ambigua*, in 1985 *Chlamydomonas* sp., *Scenedesmus quadricauda*, and *Stephanodiscus* spp., and in 1987 *Stephanodiscus astraea* (= *S. niagarae*), *Scenedesmus quadricauda*, *Chlamydomonas* sp., *Anabaena* sp., *Pediastrum* spp., *Staurostrum gracile*, *Fragilaria capucina* and *Melosira ambigua*. There are two interesting things about this species composition. First, one of the predominant species, *Pediastrum duplex*, has otherwise only been found in Oswego Lake, and second, the abundance of *Fragilaria capucina*, *Scenedesmus quadricauda*, and *Staurostrum gracile*, which are all otherwise relatively rare summer species in Oregon. The latter species are, however, rather common in the hard water and high alkalinity eutrophic lakes of the American Midwest (Wetzel 1975).

Although **Dorena Reservoir** was not analyzed for trace metals, its sedimentation rate was calculated. Dorena Reservoir was created by the Corps of Engineers in 1949 by damming Row River about 11 km upstream from its confluence with the Coast Fork of the Willamette River. The reservoir had an original maximum depth of about 30 m although this research found that it is rapidly silting in. Its area at full pool is 745 ha and it drains a 655 km² watershed which was originally entirely forested with Western hemlock and some Douglas fir. The forests have been extensively logged and much erosion has occurred as a result. The watershed is underlaid by Western Cascade andesites between 35 and 45 million years old. Dorena is a soft water, low alkalinity, oligotrophic lake (summer P concentration of 3 µg·l⁻¹, Secchi disk reading of 4.8 m, and chlorophyll *a* values of 0.7 µg·l⁻¹). One unusual characteristic of this body of water is the relatively large amount of Hg present due to large cinnabar deposits in the area. The water residence time is about a seventh of a year. In September 1981, the five predominant phytoplankton species were *Rhodomonas minuta* (~74.5%), *Ankistrodesmus falcatus* (8%), *Dinobryon setularia* (7%), *Cryptomonas erosa* (2.3%), and *Synedra ulna* (1.2%).

c. The Cascades Ecoregion

This ecoregion is the most rugged one to have been sampled in this study. It consists of two natural physiographic subunits, the Western Cascades and the High Cascades, volcanic mountains of Miocene and Pleistocene/Recent origins, respectively. Elevations range from near sea level in the Columbia River Gorge to over 3000 m. Typical elevations are between 600 and 2100 m. Average annual precipitation is between 150 and 250 cm. Unlike in the previous two regions discussed, much of it falls as snow. Again the precipitation maximum is during the winter, though summer rainstorms are common. Evaporation rates vary between 45 and 75 cm per year with the elevation being the major determining factor. The remaining natural vegetation cover are dense forests. At lower elevations the common trees are Douglas fir, noble fir, Pacific silver fir and western white pine in drier locations. Western hemlock and western red-cedar are important climax species. Mountain hemlock, subalpine fir, and Englemann spruce are common at higher elevations. Understory vegetation includes vine maple, rhododendron, huckle-, black- and salmon-berries, Oregon grape, and salal. This vegetation is much heavier in the Western Cascades than in the High Cascades, but the Western Cascades have been very heavily logged over in the past fifty years (>70% of the National Forests throughout this subregion). Above the timber line there is little vegetation as much of this zone is composed of recent lava flows; however, bent and blue grasses as well as fescue and sedges are found in alpine meadows along with various wild flowers. The soils originate mostly from volcanic material of various types including breccias, tufts, pumice, andesitic rock and basalt. There are some soils which have originated due to glacial activities, but these are very limited in extent.

Lakes are very common in the High Cascades subregion due to both glacial and volcanic processes. The largest number of lakes cored and lakes analyzed for trace metals are from this ecoregion, 11 and 7, respectively. The water chemistry of the sampled lakes was very similar from lake to lake. With the exception of Crater Lake, all of the lakes were soft water with low alkalinities, and most of them were rather oligotrophic in nature. One of the two mesotrophic lakes analyzed, Lake of the Woods, had a summer P concentration of $17 \mu\text{g}\cdot\text{l}^{-1}$, while summer epilimnetic P in the eutrophic Suttle Lake averaged 40

$\mu\text{g}\cdot\text{l}^{-1}$. These two lakes had higher trophic conditions than the others sampled due to heavy human usage and inadequate sewage treatment. Not all of the oligotrophic lakes were oligotrophic for the same reason, i.e., a lack of P, however. Blue (Jefferson Co.), Lava, Todd, and Crater Lakes are not P-limited, the only ones sampled in this study (along with the unanalyzed Fish Lake from Jackson Co.) and four of only seven mentioned by Johnson, et al. (1985). The four unanalyzed lakes from this ecoregion were not included for several reasons. The cores from Lost (Hood River Co.) and Fish Lakes were lost before analysis, while those from Hosmer and Devils were excluded because of the lack of a thermocline and being temperature, not nutrient-limited, respectively.

Three lakes in the Santiam Pass area were sampled in this study, **Big Lake** at the crest of the pass by Hoodoo Butte, **Blue Lake**, a deep maar in the next watershed eastward, and **Suttle Lake**, a glacial scour lake one km downstream from Blue Lake. These three lakes, which are close enough for all three to be easily cored in a long afternoon, typify the diversity of the lakes of the High Cascades. Big Lake is ultraoligotrophic with $2\ \mu\text{g P}\cdot\text{l}^{-1}$ despite heavy use from a Forest Service campground and some use from a church camp on the southeast shore as well as a scattering of summer residences around the southwest shore. Blue Lake is a very deep (95.7 m), oligotrophic lake with a high P concentration ($29\ \mu\text{g}\cdot\text{l}^{-1}$), while Suttle Lake is eutrophic at a P concentration of $40\ \mu\text{g}$ per liter. Big Lake has a maximum depth of 23.5 m, a surface area of 77 ha, and an approximate watershed of about $7.5\ \text{km}^2$. The entire watershed region is composed of permeable volcanic rock (a gray andesite according to Alt and Hyndman (1978), though personal observation indicates that it easily weathers to red), so the watershed area is not an exact measurement. The origin of Big Lake was either glacial scouring of the soft volcanic rock or, more likely, lava dams from Hoodoo and Belknap. Blue Lake is a volcanic maar with an age of about 3500 years. It has an area of 22 ha and a drainage basin of 43 square kilometers. Suttle Lake, with a maximum depth of 23 m and an additional 10 square kilometers of watershed over that of Blue Lake, which it is joined to by Link Creek, originated from scouring by an alpine glacier during the Pleistocene. The lake is bounded by a terminal moraine on the northeast and by a low lateral moraine to the southeast. Both Blue and Suttle Lakes also overlie permeable volcanic rock (the same general type as

beneath the watershed of Big Lake). The watersheds of all three lakes are covered by coniferous forests (70% of the total for Big Lake, >90% for Blue and Suttle Lakes). Most of the trees around Blue and Suttle Lakes are lodgepole pine which are presently dying, while the forest surrounding Big Lake has more subalpine species present. The second largest component of Big Lake's watershed is bare lava from the eruption which formed Hoodoo Butte. In addition, there was a large forest fire west of the lake in 1967 which burned off about 3 square kilometers of the lake's watershed, although this is now largely covered by subalpine flowering vegetation. There is a small marsh at the far north end of Big Lake as well. The elevations of Big, Blue and Suttle Lakes are 1416, 1052, and 1048 m, respectively. The retention times are approximately 2.4, 0.2, and 0.3 years. Much of the input into Blue Lake is due to springs, possibly of a hydrothermal nature (Johnson, et al. 1985; Priest 1988 personal communication). The phytoplankton communities are dominated by *Chromulina* sp. and *Oocystis pusilla* in Big Lake, *Ankistrodesmus falcatus*, *Tribonema* sp., and 12 species of diatoms, primarily *Synedra rumpens* and *S. radians* (6.5% together), 5 species of *Nitzschia* (7.2% combined), and *Asterionella formosa* (2.7%) in Blue Lake, while in Suttle Lake, there are 20 species of diatoms as well as 8 species of other types of phytoplankton, including nearly all of the species found in Blue Lake. The predominant species in Suttle Lake were *Asterionella formosa* and *Tribonema* sp. in May, *Rhodomonas minuta* and *Anabaena circinalis* in July, and *Stephanodiscus astraea* and *Cyclotella comta* (= *C. radiosa* now) in November, 1982. Big Lake was sampled at two different locations, Station 1 in the deep hole in the southwestern part of the lake and Station 2, up on the northern shelf (Figure 4); the other two lakes were just sampled at the deepest part of the lake.

Four lakes along the Cascade Lakes Highway, southwest of Bend, were cored in this research, and two, Todd and Lava, were analyzed for sedimentary trace metals. (The other two were Hosmer and Devils, which were dropped for the reasons previously mentioned.) Both **Lava** and **Todd** are soft water, low alkalinity mesotrophic to oligotrophic lakes with long retention times (1.3 and 0.6 years) and high summer phosphorus concentrations (530 and 63 $\mu\text{g P}$ per liter, respectively). Consequently, it is very likely that these two lakes are not P-limited. These two lakes develop thermal stratification in the summer and

Figure 4. Bathymetric map of Big Lake indicating sampling stations.

had relatively warm epilimnions (20 and 15 °C at the time of their sampling by Johnson, et al 1985, 17.5 °C in August 1987 and 18.5 °C in September 1986 during this effort). Lava Lake is 10.4 m deep, 149 ha in surface area, and has a 21 square kilometer watershed, while Todd's basic physical parameters are 18.3 m, 11.7 ha, and 2.2 square kilometers. The elevations of the two lakes are 1445 and 1875 m above sea level (Lava and Todd respectively). The watershed of Lava Lake is forested (> 92%) on top of lava flows from the Kwoh Butte section of Bachelor Butte east of the lake, dating from either the 9000 or 12,000 yrs BP eruptions (Wood and Kienle 1990), and High Cascades gray andesites to the west and south. The lake formed as a result of these Bachelor lava flows (Johnson, et al. 1985). The Todd Lake watershed is located on the southeast flank of South Sister; the lake itself is just over 10 km from the top of the mountain. Todd Lake lies in a glacial scour on top of andesitic rock. The watershed is 85% forested and there is an alpine meadow at the north end of the lake (an additional 10% of the watershed's area). The common phytoplankton of Lava Lake in August 1982 included *Chromulina* sp.(73%), *Anabaena flos-aquae* (9%), and *Rhodomonas minuta* (6%). The commonest diatoms from that sample were *Melosira granulata*, *Pinnularia* sp., and *Fragilaria construens* (all <1%). A 64 µm mesh net plankton sample from Lava Lake taken in August 1992 was dominated by a bloom of *Asterionella formosa*. The common phytoplankton species of Todd Lake, collected during the same week of August 1982 as the earlier Lava Lake sample, were *Rhodomonas minuta* (50%), *Anabaena planctonica* (36%), and *Dinobryon divergens* (7%). The only diatom observed in that sample was *Fragilaria construens* (~1%).

Two lakes in the southern Oregon Cascades, just south of Mt. McLaughlin, were cored as part of this study, Fish Lake and **Lake of the Woods**. The cores from Lake of the Woods were analyzed for trace metals; those from Fish Lake were not due to a storage problem. Lake of the Woods is a large (464 ha), popular, mesotrophic lake. There are two large Forest Service campgrounds, a resort, three organizational camps, and over 200 summer residences along its shores. Many of these are also occupied during the winter as the opportunities for winter sports, including ice fishing, are very good in this area, and access to this lake is enhanced by its relatively low elevation (1508 m) and location adjacent to a major all-weather highway through the Cascades, Oregon 140. The

lake's trophic status is due in part to its relative shallowness (mean depth of 8.1 m, maximum depth of 16.8 m), and to the heavy usage the lake and surrounding watershed receive (the resident human population resulting from its heavy use has been estimated to be equivalent to about 350 people according to an unpublished Forest Service study). Over 90% of the 63 square kilometer watershed is covered with coniferous forest. The non-winter phytoplankton assemblage is dominated by the diatoms, *Synedra radians* (~31%), *Achnanthes minutissima* (~10.5%), *Fragilaria construens* (4.3%), and *Asterionella formosa* (2.5%), and by the cyanophyte, *Anabaena flos-aquae* (9.2%). The watershed of this lake is underlain by Cascade andesites like that of all other lakes in this ecoregion. The retention time for water in Lake of the Woods is 2.2 years.

The final lake sampled in the Cascades Ecoregion was **Crater Lake**, the seventh deepest lake in the world with a maximum depth of 589 m (Edmondson 1966, Hutchinson 1957) located at an elevation of 1882 m (the rim road is over 300 m above the lake, thus direct access to the lake, hence the possibility of limnological investigations, has been limited until recently). The lake has a surface area of 5317 ha with a watershed area of only about a third more (roughly 6500 ha, or 65 km²). The residence time is estimated to be 150 years. The lake originated as a caldera from the collapse of Mt. Mazama, a typical High Cascades andesite volcano, during a series of violent explosions, climaxing about 6600 years BP. as dated by ¹⁴C (Cranson 1982, Johnson, et al. 1985). The lake possesses a significantly different water chemistry from other Cascade lakes. Although it has soft water, its alkalinity is much higher than the other lakes sampled in this ecoregion. Chloride and sulfate concentrations are also somewhat elevated. It has been hypothesized by Collier and Dymond that this is due to the presence of hydrothermal springs at the bottom of the lake in the south basin (Dymond and Collier 1990). However, several geologists, including the past head of the state geothermal program, vigorously disagree with Collier and Dymond on the possibility of hydrothermal springs within the lake (Priest 1989 personal communication). The data to date are inconclusive with respect to elevated temperatures at the bottom of the lake. While there is clear elevation of bottom water temperature (Collier, et al. 1990), the amount is less than the geological definition of required for hydrothermal springs (Priest 1989 personal communication). However, water chemistry samples and

photographs taken of sites within the south basin clearly support the Collier and Dymond hypothesis (Dymond and Collier 1990) as the water chemistry is similar to that of Myvatn, a large volcanic spring-fed lake in northern Iceland (Dickman, et al. 1993, Jónasson 1993).

The biology of this oligotrophic lake is also somewhat unusual. The lake possesses a very simple limnetic (a truly pelagic?) ecosystem with only two species of fish, two species of crustacean zooplankton, and nine species of rotifers representing all animal life within the water column proper (G. Larson 1989 personal communication, Karnaugh 1990). The phytoplankton assemblage is much more complicated than that with over 150 species found (Larson 1984, Larson and Geiger 1981, Debacon and McIntire 1991), 90% of which are diatoms including 15 species of *Nitzschia*. Less than 10 of these species are ever dominant however (Larson 1984). *Nitzschia gracilis* is the predominant species in the top 20 m of the lake (Larson and Geiger 1981, D. Larson 1984, 1985 personal communication). The diatom, *Stephanodiscus hantzschii*, predominates below 180 m, while *Tribonema* sp. is commonest between 80 and 120 m, the zone of maximum biological production in the lake. Other common surface phytoplankton species include the diatoms, *Achnanthes minutissima*, *Asterionella formosa*, *Synedra ulna chaseana*, and *Nitzschia frustulum*, the ubiquitous flagellate, *Rhodomonas minuta*, and the green alga, *Mougeotia* sp.

Recently the lake has been suffering from an optical deterioration (Secchi disc depths decreased from 38 to 26 m between 1937 and 1982, Larson 1984) which is believed to be associated with increasing populations of *Nitzschia gracilis* in the top 20 m of the lake (D. Larson 1984, et al. 1990). An alternative possible cause for some of the observed changes in Secchi disc depth is that populations of one species of fish, the kokanee, oscillate widely due to irregular recruitment, and so drives population changes in the larger zooplankton, *Daphnia pulicaria*. It is believed that these changes may influence composition of the phytoplankton assemblage (G. Larson 1993 personal communication). Further details on the origin and natural history of the lake and surrounding National Park can be obtained from Cranson (1982), while further information about the ecology of the lake is available from Drake, et al (1990).

d. The Blue Mountains Ecoregion

The Blue Mountains Ecoregion consists of several old mountain ranges stretching from the center of Oregon to its northeast corner. The ranges covered include the Blues proper, the Ochocos, the Wallowas, the Strawberries, and the Aldriches. The different ranges are divided by fault valleys and synclinal basins with several intermountain plateaus as well. The mountains are composed of Mesozoic, primarily Triassic, volcanic rocks, mostly of an andesitic nature. Other sources include Jurassic and Triassic sedimentary rocks and some serpentine and other metamorphic rocks near John Day (Alt and Hyndman 1978). Much of the valleys and foothills have been overlaid with the Miocene Columbia flood basalts, although outcrops of older rocks are common. The elevations of this ecoregion are typically 900 to 1000 m in the lower valleys and 2000 to 3000 m high mountains. Vertical changes in relief are frequently in the range of 300 to 900 m. Precipitation varies from 25 to 50 cm in the valleys to over 100 cm per year in the mountains. Evaporation is between about 70 cm per year in the mountains to over 110 cm in the valleys. The mountains originally were covered with mixed coniferous forests; the species composition changed with elevation and available amount of moisture. One forest assemblage is that of grand fir/Douglas fir, another of ponderosa pine, and a third of Englemann spruce/grand fir/Douglas fir. Stands of larch and lodgepole pine are also found. In the valleys and foothills, the original vegetation was sagebrush/wheatgrass steppe and wheatgrass/bluegrass grassland. The entire ecoregion is heavily grazed by livestock (much of it overgrazed according to Omernik and Gallant 1986), and the forests have been logged moderately. Some of the area is also used for growing small grains and hay. More than any other region of Oregon, the Blue Mountains ecoregion looks like the stereotypical "Western landscape" of Hollywood (and several Westerns, including "Paint Your Wagon," and "Bend in the River" have been filmed there). The soils, though fertile, tend to be thin and are typically derived from igneous rocks. Soil formation from its parent rock appears to be slow in this ecoregion, probably due to the lower precipitation.

Glacially-derived lakes are common in the mountains and reservoirs are found in both the mountains and in the valleys. Six lakes were successfully cored in this study, two natural lakes and four reservoirs. Five of these were in

the Blue Mountain ecoregion proper; these were Magone, Wallowa, Ochoco, Walton, and Morgan; the two natural lakes were Magone and Wallowa. The sixth lake, Haystack Reservoir, is located on the boundary between the Blue Mountains and the Columbia Basin ecoregion. Only Walton and Morgan were analyzed for sedimentary trace metals, although the Wallowa cores have been saved. **Walton** is a small (7.3 ha) reservoir in the Ochocos at an elevation of 1585 m, located 50 kilometers east of Prineville. The watershed area is only 2.2 square kilometers; it is 90% covered by an open pine forest. The maximum depth of the lake is 6.4 m near the dam face. Walton Lake's retention time is 0.5 years. The reservoir was built in the 1940's for public recreation, and as there are few lakes in this area, has been quite popular. (The maximum depth of sediment found in Walton Lake during this research was 6-7 cm in thickness for a sedimentation rate of 1.6 mm per year; the break to drowned turf was quite distinct). The lake is eutrophic by the criteria of this thesis (39 $\mu\text{g P}$ and 3.2 $\mu\text{g chlorophyll } a \cdot \text{L}^{-1}$), and the chemical composition of the water is soft with a high alkalinity, like Crater Lake. The predominant phytoplankters in July 1982 were *Aphanizomenon flos-aquae* (22%), *Fragilaria construens* (21%), the ever present *Rhodomonas minuta* (20%), *Ankistrodesmus falcatus* (18%), and *Sphaerocystis schröteri* (7%). In addition to *F. construens*, other diatoms included *F. pinnata*, three species of *Nitzschia*, a *Synedra* species, *Navicula capitata*, and the widely distributed *Amphora ovalis*.

Morgan Lake is another small (24.3 ha) reservoir. It is located 8 km southwest of LaGrande on top of a high, steep-sided butte overlooking the city at an elevation of 1266 m (by comparison, the elevation of La Grande is only 850 m). The reservoir is in a slight depression (the maximum depth of the reservoir is 7.9 m) of the flood basalt covering most of the immediate area, excepting the city of LaGrande which is on a Pleistocene lake bed. The natural drainage basin is only about three times its surface area; however, a canal diverts water from Sheep Creek to the southeast and west of the lake. The total watershed area is 11.4 km² and two-thirds of it is covered with open pine forest while the remainder is rangeland. The water in the lake is soft and its alkalinity is low overall, although rather high for lakes in this area. The lake is eutrophic due to livestock grazing upstream and a seasonally large duck population. The reservoir is primarily managed for the waterfowl and general

public recreation, though facilities here are much poorer than at Walton Lake. The dominant phytoplankton species in July 1982 were *Chromulina* sp. (74%) and *Rhodomonas minuta* (19%). The only common diatom observed in this sample was *Stephanodiscus astraea minutula* (1.3%, now = *S. minutulus*).

e. The Siskiyou Ecoregion

Along with the previous ecoregion, the Siskiyou have some of the oldest surface rocks in the state of Oregon as well as relatively large amounts of valuable hardrock minerals, including several metals such as nickel (the only commercially valuable nickel mine in the U.S. is located in this ecoregion) and chromium, as well as some gold deposits, jade, and small amounts of platinum and tungsten (Alt and Hyndman 1978). Placer gold mining is still being done here (Omernik and Gallant 1986). The largest amount of surface outcroppings of metamorphic rocks found in Oregon occur in this ecoregion, including blueschists and eclogites. The Siskiyou are geologically part of the California Coast Range (Alt and Hyndman 1978), which is characterized by the presence of large amounts of metamorphic blueschist (Tarbuck and Lutgens 1984) though their vegetation is Sierra Nevada (Omernik and Gallant 1986). Blueschist is formed by high pressures occurring deep within a subduction zone; the rock in this range was exposed after a change in the plate boundary (Tarbuck and Lutgens 1984). The blueschist and eclogites are found within large quantities of serpentine, along with much smaller amounts of red garnets. The oldest surface rocks in Oregon, the Abrams schist, occur just west of Squaw Lake, one of the three lakes sampled in this ecoregion. In addition to the metamorphic rocks, other common surface rocks found in the Siskiyou include sedimentary rocks dating from the Mesozoic, and granitic intrusions, all older than 150 M yrs BP (Alt and Hyndman 1978). The physiography of this ecoregion is characterized by steep, highly dissected mountains with narrow valleys terminating in alluvial fans. Elevations range between 240 m in the valleys to over 2100 m. Changes in local relief is often over 600 m. In order of abundance, the different soils of this area are derived from sedimentary, metamorphic, and granitic parent material (Omernik and Gallant 1986).

Climatically this ecoregion is intermediate between a warm, moderately rainy coastal region and a high, but dry, mountainous area. The average

annual precipitation is about 45 cm in some of the valleys, but can attain 200 cm in the mountains. The annual evaporation is typically between 70 and 80 cm, but this is exceeded in some of the southern valleys. The precipitation primarily occurs during the winter. The summers are typically very hot for Oregon and dry. Forest fires have been a severe problem in recent years with the increased summer temperatures and winter drought conditions that have characterized the weather over the last seven years except 1992-93 in southwestern Oregon. The current vegetation cover is mixed coniferous forests in the mountains with Douglas fir, ponderosa, sugar, and lodgepole pines, incense-cedar (commoner in moister habitats), white fir and mountain hemlock found. At lower elevations, canyon live, California black, and tan oaks as well as madrona are common. Common shrubs include manzanita, poison oak, blackberry and Oregon grape. The valley floors originally had mixed oak forest and prairie vegetation. The latter was typified by wild oats, fescue and brome grass. Though thickly vegetated, outside of the higher slopes, this ecoregion's forests are more open than any previously discussed. Logging is the principal industry here; however, some of the clearcuts have not regenerated during the last 20 years even after multiple replanting (Perry, et al. 1990). Small grains, hay, and livestock grazing are important activities on the lower slopes, while truck farms and orchards are important activities on the valley floors (For example, the Medford area produces the largest quantity of pears commercially grown in the U.S.).

Lakes in this area, outside of recently constructed reservoirs, are very scarce. There are only five named natural lakes in the south half of the Rogue River National Forest and a similar number in all of the Siskiyou National Forest. Mountain lakes generally form due to one of three processes, two major and one minor (Hutchinson 1957; Johnson, et al 1985). These are glacial scouring and morainal development at the ends of alpine glaciers; volcanic activities which form calderas, maars, and lava-dammed drainages; and from landslides. Glaciation was very limited in this area, so there are only a very few high alpine lakes formed due to glaciers in the Siskiyou (Bolan Lake is one of the few formed this way here). Since the Siskiyou are largely composed of metamorphic rocks or Mesozoic sediments and folded volcanic rocks, there has been no relatively recent volcanic activity in the Siskiyou to form any lakes.

The final, minor, process, landslides, is also less likely to occur in the Siskiyou than in any other mountain range in Oregon because metamorphic rocks are much harder than igneous or sedimentary rocks, and so are much less likely to break and fall into a valley when an earthquake occurs. Since none of these processes occur to any extensive degree in this ecoregion, lakes in the Siskiyou are quite rare.

Three lakes were successfully cored in this ecoregion and one, Squaw, was analyzed (two more, Selmac and Agate Reservoirs were attempted but very poor samples were collected). Cores from a second, Bolan, are still available for analysis. The three lakes sampled were Squaw, eight km east of Applegate Reservoir and three km north of the Oregon-California border, Bolan, about 30 km southeast of Cave Junction and less than a kilometer north of the Oregon-California border, and Emigrant Reservoir, 10 kilometers southeast of Ashland. Access to the first two lakes is *very* difficult. Squaw lies at the end of a rough gravel road which first skirts the east side of Applegate Reservoir, then winds its way along Squaw Creek for approximately nine km after leaving Applegate Reservoir. **Bolan** lies at about 1800 m in elevation. It is reached by driving about five km on a Forest Service road which runs on top of a high saddle on the state border (about 1000 m down to California and over 500 m down to Oregon). At the end of the saddle, the road drops 50 to 100 m to the north and turns a ridge, then it essentially disappears about half a kilometer short of the tiny Forest Service campground there. Bolan is an oval cirque lake with a maximum depth of 12 m and an estimated area of 13 ha. The drainage basin is only about twice again the area of the lake and it is either forested or bare rock outcrops. There is a large talus slope just south of the lake. The conductivity (i.e., total dissolved solids) is 35 μ mhos/cm, which is comparable to Lake of the Woods (at 27) and much lower than Squaw's 205. This value indicates that Bolan is a soft water lake. The summer Secchi disc depth was >10.0 m, indicating oligotrophic conditions. No phytoplankton samples have been analyzed from this lake.

Big Squaw Lake is the largest natural lake in the Siskiyou Mountains. It is 18.6 ha in area, with a maximum depth of 36.9 m, a watershed area of 47 km², and a retention time of 1.5 years. It is unusually deep for a lake of its size (Johnson, et al. 1985). The lake appears to have been caused by a landslide

slumping south across the Squaw Creek ravine at the southwest corner of the lake. Given the relative deepness of the lake to its area and the very steep sides of the lake, its formation appears to have been quite recent as when lakes fill in they rather quickly form a much flatter bottom than Squaw possesses (Davis, et al. 1985). The lake was probably formed as the result of one of the last four major Cascadia subduction zone earthquakes which occurred 300 plus, 800, and 1150 yrs BP (Darienzo 1991), or due to the same one that formed Loon Lake in the Coast Range (1460 yrs BP - Johnson, et al. 1985). Darienzo (1991) noted that the 800 yrs BP quake produced a much smaller tsunami than the other five of the last 2500 years, so it not likely to have been the one which formed Big Squaw. A long enough core for an accurate date of origin was not obtained however. The depth and area have been increased by a small (3-4 m high) dam across the mouth of the creek. Although difficult to get into for sampling, it is not at a particularly high elevation (only 916 m, Applegate Reservoir is at 606 m). Besides its depth/surface area ratio, the general scarcity of lakes in the Siskiyou, and its proximity to the Abrams schists, Squaw Lake has several other peculiarities. The most notable one is the high abundance of galena and Fe pyrite along its shoreline. Another is its water chemistry, very hard and quite alkaline. Its trophic state is low, oligotrophic to early mesotrophic. *Cryptomonas erosa* (52%), *Rhodomonas minuta* (18%), and *Ankistrodesmus falcatus* (also 18%) were the predominant phytoplankton species in July 1982. The only diatom observed by Sweet was *Nitzschia* sp. (<1%). The extreme scarcity of diatoms in this lake is supported by the sedimentary diatom data collected here as their absolute abundance quite low. I believe that this lake, while probably not unique, is certainly one of the most unusual lakes to be found in Oregon.

The remaining lake successfully cored in this ecoregion, **Emigrant Reservoir**, was sampled several times, though its sediments were never analyzed. It is a large (339 ha), deep (48.8 m) eutrophic reservoir formed in 1926 when Emigrant Creek was dammed for irrigation near Ashland. It is the lowest montane lake sampled in this study, having an elevation of only 663 m. The reservoir is located on white sandstone deposited on the eastern margin of the Klamath-Siskiyou about 50 M yrs BP (Alt and Hyndman 1978). The natural drainage is mostly off of the Siskiyou. However, when the Bureau of Reclamation

raised the dam in the late 1950s, it also developed an interbasin transfer system which diverts water from the Klamath River Basin into Emigrant Reservoir as available and needed. Consequently, although the watershed has a clearly defined area (159 km²), and the evaporation/precipitation ratio is known, the mean retention time can not be determined. The natural watershed rock is predominantly diorite and Triassic metamorphosed greenstone with early Western Cascades andesites under the eastern part. The vegetation covering the watershed is about 72% forest, and most of the remainder, closest to the reservoir, is oak-savanna rangeland. The lake's water is soft with a high alkalinity. The major reason for interest in Emigrant is its phytoplankton assemblage, dominated by large blooms of *Aphanizomenon flos-aquae* (over 76% in July 1982). It has been hypothesized that there are large amounts of available Fe in this lake (Johnson, et al. 1985) which contribute to maintaining this natural bloom. Other common summer phytoplankton species include *Cryptomonas erosa* (5.4%), *Ankistrodesmus falcatus* (4.5%), and *Rhodomonas minuta* (3.4%); the commonest diatom is *Cyclotella menghiniana* (<1%).

f. The Eastern Transition Ecoregion

The final ecoregion sampled in this study is a transition zone, or ecotone, between the moist alpine forests of the Cascades ecoregion and the more arid steppes and deserts of the Columbia Basin and Oregon High Desert ecoregions. While elevations in this ecoregion vary from near sea level at the Columbia River to over 2100 m and relief can vary by as much as 750 m, the typical elevations of this area are between about 700 and 1600 m (the towns of Madras and Lakeview, respectively) and slopes are quite gradual. Like all of the surrounding ecoregions, this part of Oregon is underlain by Tertiary, Pleistocene, and Recent volcanic rocks. Much of the area near Bend is covered with recent (< 3 million year old) basalt flows, many of them originating from Newberry Caldera, while Cascade andesites are predominant to the west and south. There are numerous volcanic peaks from very recent cinder cones (i.e., Lava Butte near Bend, or Pilot Butte within that town) to basaltic domes like Newberry Caldera. The western part of this region is still quite volcanically active as there were eruptions of Newberry Caldera less than 2000 years ago, and Lava Butte last erupted about 1300 years ago. Geothermal prospecting is

active around the Newberry Caldera with a possible plant now being proposed for the interior of the Monument, and geothermal energy is used for heating near Klamath Falls and may soon be used in the Lakeview area. The age of igneous rocks in this ecoregion increases as one travels east-southeastward (Orr, et al. 1992). Due to the recent volcanic activity and generally dry conditions, there is little soil in this ecoregion compared to the others studied.

The majority of the precipitation falling in this ecoregion occurs outside of the summer; much of it as dry snow during winter. Precipitation is between 30 and 60 cm per year while evaporative losses are on the order of 80 to 110 cm per year. The difference is made up by drainage off the High Cascades and springs which also may come from Cascade snows. The natural lakes are all concentrated on the higher tablelands and mountains where the precipitation is greatest and evaporation the least. Open ponderosa and lodgepole pine forests dominate the vegetation of this area with bunch wheatgrass and Idaho fescue covering the understory where there is soil. Manzanita and bitterbush are common shrubs, and juniper is found in the drier areas while quaking aspen is important in riparian habitats. The major economic activities are logging, livestock raising, and outdoor recreation. The use intensity has not exceeded the area's capacity yet (Omernik and Gallant 1986).

The lakes of this area have been largely caused by volcanic processes, either directly through eruptions or by lava flows damming stream courses. The two largest lakes sampled, East and Paulina, are in the Newberry Caldera, while the Twin Lakes, west of Newberry, are maars. Delintment, the fifth lake sampled, was a reservoir built by the Forest Service in 1940 on the site of several beaver ponds. The origin of the sixth lake cored in this study, Dog Lake, west of Lakeview, is not clearly known. Gerber Reservoir, the last lake in this region to have been attempted, fills a caldera of Tertiary origin (Alt and Hyndman 1978), about 5 to 6 million years old (Orr, et al. 1992). The dam was built in 1925 across a narrow ravine having perpendicular sides naturally formed by columns of basalt. Only East, Paulina, and South Twin Lakes were analyzed for sedimentary trace metals.

East and Paulina Lakes are hard water, high alkalinity lakes. Paulina is considered to be eutrophic, while East is mesotrophic. Both lakes are large and deep; East covers 422 ha and is 54.9 m deep, Paulina is 620 ha in area and has

a maximum depth of 76.2 m. The two lakes are separated by a series of lava flows, 1.5 km wide, which divided them about 2050 years ago. They, in turn, essentially equally divide the inside of Newberry Caldera with Paulina draining 21 km² and East, 22 square kilometers. East is 1942 m above sea level, Paulina, 1930 m. While East has no surface outlet, it is likely that there is subsurface flow between East and Paulina, probably mainly from East to Paulina as there is a surface outlet of Paulina, Paulina Falls. Fifty-six percent of Paulina's watershed is forest, 26%, the lake itself, and the remainder is lava fields. East's watershed is 76% forested and 6% lava fields; the lake itself covers the rest of the area. It is believed that much of the precipitation on East's watershed actually drains out of the caldera directly without entering the lake. Retention times are 18 years for East Lake and 46 years for Paulina. The forest around these two lakes is open lodgepole and ponderosa pine with a few mountain hemlocks and scattered alder. This area has a number of interesting geological phenomena due to its history. Included on this list are the presence of geothermal hot springs along the southeast shore of East Lake and a large obsidian flow south of both lakes. Because of its interesting geology, the Newberry Caldera was made into a U.S. National Monument in November 1990. While the trout fisheries of these two lakes are quite good and the water quality of East Lake adequate, there is some concern that the increased use may harm the water quality of Paulina Lake. Phytoplankton populations in East Lake are dominated by *Dinobryon sertularia* (44%), *Rhodomonas minuta* (37.4%), and *Ankistrodesmus falcatus* (9.1%). The commonest species of diatoms were *Fragilaria brevisstrata* (0.8%), *F. vaucheriae* (0.3%), *Navicula* sp. (0.3%), *Epithemia turgida* (0.3%) and *Cocconeis placentula* (0.2%). Sixteen species of phytoplankton, eight of which were diatoms, comprised 98.4% of the total numbers for three different summers. The phytoplankton of Paulina Lake were mainly *Anabaena flos-aquae* (67.9%), *Rhodomonas minuta* (11.8%), *Cyclotella comta* (7.4%), and *Asterionella formosa* (3.5%). There were four other common diatoms, *Nitzschia volcanica* (1.3%), *F. brevisstrata* (1.2%), *Stephanodiscus* sp. (0.7%), and *N. dissipata* (0.7%). The uncommon diatom species, *F. pinnata*, was also found.

The final lake analyzed from this ecoregion was **South Twin Lake**, a small (40 ha), shallow (17.7 m) maar located just east of Wickiup Reservoir,

southwest of Bend and 16 kilometers west of La Pine. The lake constitutes 57% of the drainage basin, as it is only 70 ha (0.7 km²) in size. The remainder is forested. Residence time for water in South Twin is 22 years. Water chemistry in this lake is somewhat odd for Oregon lakes. While it is a soft water lake, the alkalinity is quite high, similar to North Twin and Crater Lakes. Furthermore, while concentrations of chlorophyll *a* (1.0 µg·l⁻¹) and P (17 µg·l⁻¹) are low and the Secchi disc transparency is high (8.5 m), indicating that it is an oligotrophic lake; dissolved oxygen declines rapidly below 8 m, suggesting a mesotrophic status. The predominant species of phytoplankton in this lake in July 1982 were the universally found *Rhodomonas minuta* (61%), *Sphaerocystis schröteri* (16%), and *Tabellaria fenestrata* (7.2%). Other diatoms found included *Nitzschia microcephala* and *Achnanthes lanceolata*, both less than 1% of the total cell count. *Dinobryon divergens*, a phytoplankton species characteristic of oligotrophic lakes, is also found. The lake is 1321 m above sea level.

II. Methods and Materials

A. Field Methodology

1. Lake Selection Criteria

The initial criteria for selection were reasonable accessibility and the presence of a thermocline. The first criterion was strictly a practical matter rather than for any scientific reason. The second criterion was designed to maximize the probability that the sediments would not be disturbed by wind mixing as is frequently the case in non-stratifying shallow lakes. Undisturbed sediments are much more useful in determining the paleolimnology of a lake than are wind-mixed sediments (Håkanson and Jansson 1983). The existence of previous limnological work was also considered an asset. In that regard, lake selection was primarily made from the sets of the 202 lakes sampled by Johnson, et al. (1985) and those studied earlier by the U.S. Geological Survey (1973-1979).

Beyond these very general criteria, lake selection was based upon as wide a diversity of types as possible in order to fulfill the objectives stated in the rationale. The initial hypothesis as to the potential causes of differences between lakes was that they were based upon climatic regime, trophic condition, and major ion water chemistry. The set of lakes selected from was first divided based upon the general climatic regime where they were found (Maritime, Montane, and Steppe). These three groupings were then divided on the basis of trophic condition and water chemistry. The three trophic conditions were oligotrophic with low concentrations of dissolved phosphorus, oligotrophic with high phosphorus, and eutrophic with high phosphorus. Due to other chemical and geological considerations, several of the lakes actually analyzed were mesotrophic with medium levels of dissolved phosphorus. Also a few lakes without thermoclines were included to increase the diversity of water chemistry types.

Four broad categories of major ion water chemistry were found, soft/low alkalinity, hard/high alkalinity, soft/high alkalinity, and high conductivity/low alkalinity. These terms were defined as follows:

Low phosphorus: $\leq 18 \mu\text{g tdP}\cdot\text{l}^{-1}$ before the spring bloom

High phosphorus concentrations were $\geq 25 \mu\text{g tdP}\cdot\text{l}^{-1}$.

Oligotrophic: Secchi disk ≥ 5.0 m and Chlorophyll $a \leq 3.0 \mu\text{g}\cdot\text{l}^{-1}$
or Secchi disk > 3.0 m and Chlorophyll $a < 0.5 \mu\text{g}\cdot\text{l}^{-1}$

Eutrophic: Secchi disk < 3.0 m and Chlorophyll $a \geq 4.0 \mu\text{g}\cdot\text{l}^{-1}$

Soft water was $\leq 60 \text{ mg}\cdot\text{l}^{-1}$ as CaCO_3 .

Hard water was $\geq 75 \text{ mg}\cdot\text{l}^{-1}$ as CaCO_3 .

Low alkalinity was $\leq 32 \text{ mg}\cdot\text{l}^{-1}$ as CaCO_3 .

High alkalinity was $\geq 40 \text{ mg}\cdot\text{l}^{-1}$ as CaCO_3 .

High conductivity relative to alkalinity was considered to be any value in excess of the graphically derived relationship, $C = 2.2 A + 30 \text{ mg}\cdot\text{l}^{-1}$, where C is conductivity in $\mu\text{mhos}\cdot\text{cm}^{-2}$ and A is alkalinity in $\text{mg}\cdot\text{l}^{-1}$.

Of the original 36 categories theoretically present (3 climatic regimes * 3 trophic conditions * 4 major ion water chemistries), only 18 had any Oregon representatives. Within these groups, wherever possible, three replicate lakes with residence times of over one year were selected. A total of 55 lakes were finally selected and 49 were eventually sampled. As this research progressed, this list was refined into one with 36 lakes present. Among other changes, all lakes within the Steppe climatic regime and most of the reservoirs were dropped. The former group was dropped due to lack of time while the latter was dropped because many reservoirs lack a firm bottom, so could not be sampled with the coring equipment used. Following a major laboratory accident (see below) which resulted in the loss of cores from three field seasons, a subset of 21 lakes was finally analyzed with atomic absorption spectrophotometry. The final list of lakes is given in Table 2.

During the course of this research an alternative hypothesis as to the basic cause for aquatic distinctions was developed by Omernik and Gallant (1986). The eight ecoregions that Omernik and Gallant proposed were the Coastal and Willamette Ecoregions within the Maritime Climatic Regime, the Cascades, Siskiyou, Blue Mountain and Eastern Transition Ecoregions within the Montane Climatic Regime, and the High Desert and Columbia Basin Ecoregions within the Steppe Climatic Regime (Figure 2, p. 67). The largest differences between the two hypotheses were one, the relative importance of trophic conditions, and two, the importance of major ion water chemistry. A particularly good example of the latter difference was the inclusion by Omernik and Gallant of the high conductivity lakes along the coast with the soft water lakes of the Coast Range within the Coastal Ecoregion.

Table 2. The Lakes Analyzed in this Study by Climatic Regime, Ecoregion, and Water Chemistry.

Maritime		Montane	
Coastal	Willamette	Siskiyou	Blue Mts
Carter 1 ✓	Dorena Res. 2	Bolan 2	Wallowa 1
Clear (Lane) 1	Silver Creek Res. 6		
Eel 1 * ✓ Δ		Squaw 4 ✓	Morgan Res. 6 ✓
Woahink 1 * ✓ Δ	Blue (Multnomah) 7		
Munsel 1 Δ		Emigrant 7	Walton Res. 7 ✓
Cullaby 5 o	Clear (Marion) 8 ✓		Ochoco Res. 8
Mercer 5 ✓	Oswego 8 ✓		
Siltcoos 5 *		Cascades	East. Transition
Coast Range		Big 2 * ✓	North Twin 3
Ollala Res. 2 Δ		L. Woods 2/6 ✓	South Twin 3 ✓
Loon 2 * o ✓		Suttle 6 * ✓	Dog 7
Triangle 2/6 ✓			
		Todd 2 (9?) ✓	East 4/8 * ✓
		Lava 9 ✓	Paulina 8 * ✓
		Blue (Jefferson) 9 * ✓	
		Fish (Jackson) 9	
		Crater 10 * ✓	
<p>Key: 1 = high conductivity/ low alkalinity; oligotrophic/ low phosphorus</p> <p>2 = soft/low alkalinity; oligotrophic/low phosphorus</p> <p>3 = soft/high alkalinity; oligotrophic/low phosphorus</p> <p>4 = hard/high alkalinity; oligotrophic/low phosphorus</p> <p>5 = high conductivity/low alkalinity; eutrophic/high phosphorus</p> <p>6 = soft/low alkalinity; eutrophic/high phosphorus</p> <p>7 = soft/high alkalinity; eutrophic/high phosphorus</p> <p>8 = hard/high alkalinity; eutrophic/high phosphorus</p> <p>9 = soft/low alkalinity; oligotrophic/high phosphorus</p> <p>10 = soft/low alkalinity; oligotrophic/high phosphorus</p> <p>* = Lakes previously sampled for trace metals by R.W. Collier.</p> <p>o = Lakes with high concentrations of dissolved organic compounds.</p> <p>✓ = Lakes sampled in this study for analysis by AAS</p> <p>Δ = Lakes sampled in this study for analysis by INAA</p>			

2. Sediment Coring

Lake sediments were collected using a sling-operated, single piston corer. The corer was gently lowered while in the cocked position until contact was made with the sediment-water interface, then a messenger weight was dropped to trigger driving a core liner into the sediments. The corer collected the sediment sample in the same plastic liner used for storing it. The liners were made of Lexan™ polycarbonate plastic, 4 cm in diameter and 1-2 mm thick. Lexan was used since the primary objective of this research was to measure sedimentary trace metal concentrations and contamination of the sediments needed to be prevented. Since the liner was the main collection device, it also needed to be both durable and not too flexible; Lexan met these requirements. Two different corers were used during this research, a 120 cm long one, and one 60 cm long. The maximum effective sediment depths that could be sampled by these corers were 110 and 50 cm, respectively. After collection of each core, both ends of the liner were sealed with #10 black rubber stoppers, which were in turn taped down tightly by duct tape to prevent sample loss (which occurred, despite these efforts, about two to three percent of the time due to rough roads).

Crater Lake sediments were subsampled from cores collected by Drs. Robert Collier and Jack Dymond, Oregon State University College of Oceanography. These cores were collected in 10 cm diameter white plastic core liners.

The cores were collected from the deepest part of each lake in replicate. Extra cores were collected and analyzed by atomic absorption spectrophotometry from Carter (1), Clear, Marion Co. (1), Suttle (1) and Big (3). Four of the lakes, Woahink, Big, Carter, and Crater, were sampled in a second location as well (See Figures 3, 4, 5 and 6).

The cores were stored upright at 4 °C until processed as refrigeration has been demonstrated to be an adequate preservation technique for maintaining different trace metal fractions in their original state (Rapin, et al. 1986). The only exceptions to this procedure were the cores from Clear Lake, Marion Co., Carter, and Morgan. The bottom temperature in these lakes at the time of collection was between 15 and 25 °C, so cores from these lakes were stored at room temperature. After the failure of the laboratory refrigeration system in 1988, thirteen of the lakes were re-sampled in 1988 and 1989: Big, Blue,

Figure 5. Bathymetric map of Carter Lake indicating sampling stations.

Figure 6. Bathymetric map of Crater Lake indicating sampling stations.

Suttle, East, Paulina, Todd, South Twin, Walton, Woahink, Mercer, Eel, Loon, and Oswego. Extra cores were also taken from Clear Lake, Marion Co. after it was discovered that drying altered the chemical fractionation. Samples for Lava, Squaw, Lake of the Woods and Triangle were run using the “cooked” cores (temperatures after the failure attained 35 °C).

3. Water Chemistry and Phytoplankton Sampling

Water samples were collected using a 2 l Van Dorn water sampling bottle made of PVC plastic with rubber stoppers and sampling tube. The only metal on the Van Dorn bottle was on the outside, i.e., the line clamp, the trigger mechanism, and the sampling tube clamp. Epilimnetic water samples were taken from 0.5 m below the surface and hypolimnetic samples were collected from approximately one meter off the bottom. The water samples were put into acid-washed polyethylene or glass bottles. After returning from the field these samples were kept in reduced lighting and at similar temperatures to what they had been collected at. Sample filtration through 0.45 μm pore size Millipore filters was done at the end of each field season. The samples were then acidified to a pH of 2.0-2.5.

Phytoplankton samples were collected from 0.5 m below the water surface of each lake with the amber plastic container that each sample was stored in. One to two ml of Lugol's solution was then added to each sample to preserve it. More Lugol's was added during the storage period as needed.

Ancillary measurements of Secchi Disk transparency and surface and bottom water temperatures were also taken from each lake as was a zooplankton sample. The surface pH was measured after returning to the lab, usually in one to three days after the water sample was collected.

B. Laboratory Techniques

1. Initial Core Processing

Each core was extruded from the Lexan liner onto a plastic sheet after being first measured to the nearest mm in length. The floc layer was decanted before extruding the core proper. During extrusion the maximum compression that occurred among all cores measured was less than two percent. Following extrusion the core was segmented into approximately one cm thick segments

with the floc, 1-2 cm from the original surface, 2-3 cm, 5-6 cm, 10-11 cm, 20-21 cm, and the bottom one cm segment always being saved. Occasionally where distinctive features were found in the core outside of the standard depths, additional segments were also kept. These extra segments were typically at an event horizon, usually a volcanic ash or tephra layer.

The 2-3 cm, 5-6 cm, and 20-21 cm segments (henceforth referred to as the 2, 5, and 20 cm segments) of each core were processed for trace metals. One third to one half of each segment, depending upon whether or not the fractionation procedure (discussed below) was to have six or eight replicates, was immediately put into a pre-weighed beaker and weighed to the nearest mg, then Nanopure™ distilled, de-ionized water was added to the beaker to prevent drying, immediate oxidation, or loss of pore waters.

The remainder of these segments and of all others that were taken from each core were placed in pre-weighed crucibles, weighed, then dried in an oven at a temperature of 50-60 °C for a minimum of 24 hours. The percent dry weight determined for the 2, 5, and 20 cm segments was then used to calculate the initial amount of dry sediment used for trace metal analysis. The dried sediment from the three main depths was divided into portions for later sedimentary diatom identification and enumeration, for percent loss on ignition, and for neutron activation analysis when and where possible.

The percent loss on ignition at 550 ± 10 °C was measured for all samples where trace metals had been measured to determine the amount of organic material present in the sediments. In addition, at least two samples from each lake had the percent loss on ignition at 950 ± 100 °C measured. The latter loss, corrected for the approximate percent water lost from clays in the sample, is an estimator of the amount of carbonates present in the sediments (Dean 1974). Calcium carbonate decomposes at approximately 890 °C, and magnesium carbonate at about 850 °C. A 100% clay sediment will have a loss of 5% by weight of water, hence any fine grained sediment with a loss in excess of 5% was classified as having at least X - 5 % carbonate.

2. Chemical Fractionation Procedure

The sequential fractionation procedure used in this research is based upon methodologies developed by Engstrom and Wright (1984) and Tessier, et al.

(1979, 1980, 1985), but was somewhat modified from their original methods. The sediment samples were first stirred with a magnetic stirrer and teflon-coated stirring bar for at least 30 minutes in a 1 M solution of MgCl_2 . The amount of MgCl_2 used was estimated on the basis of the wet and expected dry weights. A minimum of 10 ml of solution per gram of estimated dry weight was used, or 25% greater than determined to be necessary by Tessier, et al. The extra did not affect anything other than the final volume of the extract, and it insured that the ion exchange process went to completion. The mixture was then centrifuged at 6000 rpm for two hours, then the supernatant was poured off into a graduated cylinder and allowed to settle for at least 24 hours. The original technique of Tessier, et al. called for a centrifuge speed of 10,000 rpm for half an hour. This modification was required because the centrifuge available could not exceed 6000 rpm. Since gravity and acceleration follow a squared relationship, an increase in time in excess of $(10/6)^2$ times the original amount of time was calculated to be the best correction to duplicate the original force used with the safety factor of the 24 hour settling time added onto the resulting supernatant. This supernatant fraction, the MgCl_2 extraction, represents all of the metal ions present in porewater or which are loosely adhered to the mineral grains. This extraction, and the following three, are functional extractions, not absolute, pure, or completely specific physiochemical extractions (i.e., there are degrees of adhesion by different ions and this method may either not get all of the amount adhering to different minerals, or it may leach out some metals from other sedimentary components. However, the particular method selected was among the "gentlest" ones available, and the duration was maximized in order for the extraction to achieve completion).

The centrifuge pellet from the first extraction was treated with 25 ml of 30% H_2O_2 per gram dry sediment weight, boiled down to 25 ml total volume, then rinsed and boiled down five more times using Nanopure water to rinse with. The solutions were not allowed to boil dry, and after some initial splattering problems, the heat and amount of liquid remaining in the glass beaker were regulated to minimize losses. The mixture was then centrifuged as in the previous extraction and the supernatant decanted off into a graduated cylinder for later use in atomic absorption spectrophotometry. The rinses were a new step added to this extraction to insure that oxygenation of the peroxide was

complete before the solution was added to the volumetric flasks for atomic absorption spectrophotometry. Otherwise, there was later release of oxygen after the addition of acid to the peroxide extraction, and consequent loss of liquid volume in the volumetric flasks. The trace metals from this extraction were those which should have been present either as metallo-organic compounds in the sediments or as metal sulfides in high sulfur, reduced sediments. This extraction did not break down all of the organic material present in the sediments; however, as shall be discussed later, the remaining organic material was demonstrated in this research to be metal-deficient. Thus, while again the peroxide extraction is a functional methodology, and not a completely specific reaction; it is a relatively thorough and reproducible one which apparently removes most, if not all, of the available metals from any organic matrices or compounds present in the sediments. Also this extraction apparently did not measure all of the metal sulfides as will be explained in the Discussion.

The centrifuge pellet from the second extraction was treated with 5 ml of 3 N HCl per gram dry sediment weight and boiled for an hour, then centrifuged as in the previous extraction and the supernatant decanted off into a graduated cylinder for later use in atomic absorption spectrophotometry. This extraction (as well as the centrifugation and decanting) was repeated until there was no further yellow color, due to ferric chloride, visible in the supernatant. This latter step is another modification to the Tessier extraction techniques. It was added because it is now known that ferro-manganese oxides exist in sediments as several different crystalline forms (Davison 1985, Sholkovitz 1985); at least one of which requires extensive heating in acid before it will dissolve. The HCl extraction, like the two previous ones, is a functional extraction, rather than a highly specific chemical reaction. The targets for this extraction are sedimentary metal oxides, including the abundant iron and manganese oxides, and any metal ions trapped in carbonate minerals.

The centrifuge pellet from the final HCl extraction was then dried in a pre-weighed crucible at 50-60 °C for a minimum of 24 hours, weighed, and then ashed at 550 ± 10 °C for a minimum of 24 hours, and finally reweighed. Approximately one gram of ash from the 5 cm samples only was then dissolved in 20 ml of concentrated (40-42%) HF and the resulting solution slowly evaporated in a teflon beaker under a ventilated hood. When the solution was down

to a few beads in the bottom of the beaker, 30-50 ml of Nanopure water was added and the solution was returned to the hot plate. This slow evaporation and rinse was repeated a minimum of two-four more times for each sample. In theory this method of slow extraction and repeated rinses removes all of the silicates from the residual sediment as silicon hexafluoride gas, hence removing the silicon interference to atomic absorption spectrophotometry and liberates all of the metals present in the silicates, as well as cooking off any remaining HF as fluorine gas. While the primary objective was achieved, a number of the volumetric flasks were etched by HF even after five rinses of Nanopure water.

An alternative method for extraction of the residual trace metals was initially used for several cores in parallel with the previous method. Instead of dry ashing the dried residue in a muffle furnace, the residue was wet ashed with 4 ml of perchloric acid in addition to the 20 ml of HF. This method gave significantly (95% level) lower concentrations of trace metals, on the basis of the original dry weight, for 72% of all samples measured. As a result, this method was dropped after analyses of cores from the first four lakes.

Both of the residual extraction methods produced a precipitate of metal fluorides if too much HF was used relative to the amount of silicate present. X-ray diffraction of one such precipitate from Clear Lake, Marion Co. showed a mix of six, or possibly seven, metal fluorides. However, only small amounts of iron fluoride and manganese fluoride were detected, while no fluorides of zinc, copper, cobalt, nickel, or vanadium were found in this sample. The Clear Lake precipitate was the largest produced during this research, hence, this problem was probably not a serious source of losses for the metals of interest.

In summary, the sequential extraction procedure was first with MgCl_2 , then with H_2O_2 , then HCl, and finally with HF. These four extractions functionally separated the sedimentary trace metals into 1) those metals found in porewaters or which are loosely adhering to minerals and thus easily exchangeable with the Mg^{2+} ion (hence referred to as the exchangeable fraction or Me_{Ex}), 2) easily liberated organically-bonded metals and metal sulfides (the organic fraction or Me_{Or}), 3) the metals found in metal oxides and carbonate minerals (the oxide fraction or Me_{Ox}), and 4) the residual fraction of refractory metals, mainly found as silicates or within a silicate mineral lattice (the residual fraction or Me_{Res}). The first three extractions comprise all of the metals

which are believed to be biologically available under any conceivable biological or chemical process occurring in natural waters or in the underlying sediments. Their sum is thus referred to as the total potentially available metal concentration (Me_{TA}). The last fraction (Me_{Res}) is thought to be primarily allogenic (or deriving from outside of the lake proper, though still from within its watershed) clastic debris. A summary diagram of the final methodology used is presented in Figure 7.

3. Trace Metal Analysis

a. Atomic Absorption Spectrophotometry (AAS)

Each extraction was added to five, six or eight volumetric flasks in equal amounts using an Oxford™ Auto-pipetter (for the first core, from Carter Lake, 12 volumetrics were used per extraction); six was the standard number of volumetrics used. Any remaining volume of extraction was measured and the value for the dry weight of the sample correspondingly adjusted for that extraction. After the initial core, the exchangeable, organic, and residual fractions were added to 25 ml volumetrics while the oxide fraction was added to 50 ml volumetrics. This difference was as a matter of convenience as the latter extraction tended to have higher values, hence needed some dilution. Ten ml of 25% HNO_3 per 25 ml was added to each volumetric for a final concentration of 10% nitric acid; a fixed volume of a Standard Additions solution was also added, as well as Nanopure if necessary, filling to the volume mark. Blanks of both Nanopure and 10% HNO_3 in Nanopure were included as part of all AAS runs.

Next each volumetric flask was inverted a minimum of seven times to insure complete mixing of the sample with the acid, standard addition (if any), and Nanopure. After four to twelve hours, the volume of each volumetric flask was measured to determine the accuracy of the additions. These volumes were recorded for later use as a correction factor. The most frequent correction factors were either no change or an adjustment of about 0.2% dilution.

Since many other metals were also extracted during this procedure, especially during the residual extraction, the method of Standard Additions was used to correct for the matrix effect in the sample. This effect is due to multiple interferences and/or false enhancements by other elements at the wavelength for the metal of interest. The matrix effect is analogous, but not equivalent, to

Figure 7. Extraction Methodology

$$\text{Total Available Metal Concentration} = \text{Exchangeable fraction} + \text{Organic fraction} + \text{Oxide fraction}$$

the difference between chemical activity and chemical concentration. However, like the difference between chemical activity and concentration, it is more severe with increasing amounts of total dissolved materials. Typically in this research, the matrix effect was non-existent for the organic extraction, very small for the exchangeable extraction, of varying significance for the oxide fraction, and quite high for the residual extraction. This result, however, was not known beforehand, thus all samples were processed using the method of Standard Additions.

The method of Standard Additions is a standard procedure of atomic absorption spectrophotometry (Perkin-Elmer 1976, U.S. EPA 1979). It utilizes the fact that when a known amount of material is added to an unknown mixture, the increase in the signal is proportional to the known amount. Thus by adding a set of fixed amounts to equal subsamples of the original extraction, a linear regression can be made of the signals to the concentrations of the known additions plus the unknown and the corrected concentration of the unknown extracted as the x-intercept of the regression. If there is no matrix effect, or if the interferences and false enhancements cancel out exactly, then the slope of the regression is equal to 1.00000 (i.e., it has a slope of 45°).

In this research a mixed solution of $300. \mu\text{g Fe}\cdot\text{ml}^{-1}$, $6.0 \mu\text{g Mn}\cdot\text{ml}^{-1}$, $6.0 \mu\text{g Zn}\cdot\text{ml}^{-1}$, $15.0 \mu\text{g Cu}\cdot\text{ml}^{-1}$, $4.0 \mu\text{g Co}\cdot\text{ml}^{-1}$, $15.0 \mu\text{g Ni}\cdot\text{ml}^{-1}$, and $30. \mu\text{g V}\cdot\text{ml}^{-1}$ (All specific concentrations are as the final value of SA), added at levels of 1, 2, or 3 ml $\cdot 25 \text{ ml}^{-1}$ for the Standard Additions, was used. When eight equal subsamples of an extraction were used, the replication was a complete blocked design, i.e., there were two replicates of each level, 0, 1, 2, and 3. When six replicates were used, as was the standard procedure after Blue Lake, Jefferson Co., the fifth lake analyzed, one replicate of 1 ml SA and one replicate of 3 ml SA were dropped from the complete set.

The initial atomic absorption spectrophotometer used for the first core from Carter Lake was an IL 551. Five electrical circuit boards of this machine were destroyed in a laboratory accident. Subsequently a Perkin-Elmer 305B was acquired and set up. The rest of the AAS work, beginning in October 1988 and lasting through March 1991, was done on this machine. The analog output of the PE 305B was converted into digital values by an external circuit box and the resulting signal sent to a Macintosh 512 computer.

An air-acetylene, reducing, "blue" flame was used for the AAS measurement of iron, manganese, zinc, copper, cobalt and nickel, while a nitrous oxide-acetylene, oxidizing, "yellow" flame was required for the vanadium. On average, the analysis of vanadium required as much, or more, acetylene as did the combined analysis of the other six metals. Vanadium analysis also required the addition of 2 ml of 2.47 M $\text{Al}_2(\text{NO}_3)_3$ solution per 100 ml of sample. Standard wavelengths were used for the measurement of all metals (U.S. EPA 1979); 372.2 and 392.2 nm for Fe, 279.7 and 403.3 nm for Mn, 214.1 nm for Zn, 325.1 nm for Cu, 241.0 nm for Co, 232.2 nm for Ni, and 318.7 nm for V (these wavelengths differ slightly from the U.S. EPA (1979) specifications because of a small amount of wobble in the grating selector dial of the PE 305B due to the age of the machine). A set of standards, each separately made up with 10% HNO_3 , was used for each metal.

Initially the measurement of sedimentary and water column filterable molybdenum was included in this research. With the loss of the IL AAS in July 1988, this work was no longer possible. However, prior to this research, Dr. Robert Collier at the Oregon State University College of Oceanography had measured filtered aqueous Mo from nine of the 21 lakes studied using a graphite furnace attached to a PE AAS 5500. After verifying that sampling and storage procedures used here were or equivalent to Dr. Collier's, I arranged with Coffey Laboratories of Portland, OR for them to run the water samples collected from the other 12 lakes. (The sampling and storage procedures were mid-summer epilimnetic samples from 0.5 to 1.0 m below the surface that had been filtered through 0.45 μm Millipore™ filters and then acidified [pH for RC samples = < 2.0; pH for these samples = 2.0-2.5] and stored in plastic bottles [valid values possible for up to five years, or longer - R.W. Collier 1991 personal communication; the oldest sample here was 5 years, 9 months, three others were 5 years, 8 months, and the rest were less than five years old; no systematic significant differences were noted in the values for any of the oldest samples vs. either the rest of the samples or those of Collier's].)

b. Neutron Activation Analysis (INAA)

The dried samples were first ground into a fine powder with a ceramic mortar and pestle. The mortar and pestle were washed between each sample with

95 % ethanol. Next, approximately one gram of powder was put into an ethanol-washed, dried and preweighed $\frac{1}{2}$ dram plastic vial. The vial was reweighed, then heat-sealed and placed in a labeled two dram vial. Fifteen samples from Woahink and Ollala Reservoir were irradiated in the Reed College Nuclear Reactor for one hour at 238 kW. Forty samples from Woahink, Eel, and Munsel were irradiated in the OSU Triga Reactor twice at 1000 kW, once, a "rabbit" run, for three to five minutes, and once for four hours. Another difference between the Reed College and OSU runs was that the outer vials were also heat sealed prior to the OSU runs while they were not for the Reed College run.

The samples from the Reed College run were allowed to "cool" for four and a half days, then measured at PSU with a TN-1300 Ge(Li) gamma ray detector for total Fe, Co, and As as well as the Rare Earth Elements (REE), Na, K, Sb, and Cr. The samples from the OSU "rabbit" run yielded total Mn and V, as well as Al and Mg. The longer OSU run, after "cooling" for two weeks, produced values for total Fe, Co, As, and Se as well as the REE, Na, and K. All measurements at OSU used their Ge(Li) gamma ray detector. Due to budget limitations at the OSU reactor, regulatory restrictions at the Reed College reactor, as well as a change in objectives in this research from determining the total sedimentary metal concentrations to determining the available concentrations, no further samples were analyzed for total sedimentary metals.

Spectral peak data from the Reed College run, used to produce final elemental concentrations, were analyzed on the PSU Honeywell 66/20 main-frame computer using the Geochemistry Library program for instrumentation neutron activation analysis (INAA). Manganese spectral peak data from the OSU "rabbit" run were reduced on an Apple IIe computer using the PSU INAA7 program translated into Applesoft BASIC and modified for variable wing size. All other elements from the two OSU runs were reduced by OSU Radiation Center personnel and any necessary corrections were done with a hand calculator.

4. Sedimentary Diatom Analysis

About 10-25 mm³ of dried sediment was placed into a 25 ml test tube, following the method of Van der Werff (1953). Three to five ml of 30% H₂O₂ was added to the sediment, then a few grains of potassium dichromate. After the

sample boiled and the solution changed color from purple to yellow, it was allowed to settle for two days with a distilled water rinse after one day. The supernatant was then gently poured off and the "lighter" material poured into a Batterbee settling chamber (Batterbee 1973) and dried onto cover slips. The dried sample was then mounted on a clean and brand new glass slide in Canadian balsam and, after the xylem had evaporated, it was sealed with nail polish.

Enumeration was by direct counts to species of a minimum of 300 frustules. References used were Hustedt (1930), Patrick and Reimer (1966, 1975) for the orders of Fragilariales through Naviculales, translations by C.D. McIntire from Hustedt (1930) for the genera of *Epithemia*, *Nitzschia*, and *Melosira*, and a key to the Thalassiosiraceae developed from articles by Håkansson, Stoermer, and Theriot (Vogel, paper in progress). *Nitzschia volcanica*, an epibenthic species found in Crater Lake and the two lakes of the Newberry Caldera, was identified based upon Sovereign (1958). Separation of *Fragilaria* and *Synedra* was based upon whether the striae were opposite (*Synedra*) or alternate (*Fragilaria*) following Round (1991). More than half a frustule had to be present before it was included in the enumeration with the exception of *Asterionella formosa* and *Synedra ulna* which only needed to have over a third before being included due to their large size and the severity of the cleaning procedure.

The diatoms in the treated sediments were enumerated and identified at 1000X under oil immersion using a Zeiss compound microscope. Initially each count continued until both 30 fields and 300 cells were enumerated. Due to the wide variability in the numbers of preserved frustules (the number of frustules observed varied by over two orders of magnitude from over 100 frustules per 0.18 mm diameter field to less than 100 frustules per central row of 20 mm), the first criterion was dropped after the Coastal ecoregion lakes were counted. The number of frustules enumerated was increased to a minimum of 1000 for the samples from lakes of the Cascades and Eastern Transition ecoregions.

C. Data Analysis

1. Data Reduction

The metal data produced by the AAS and transformed into digital form by the external converter was recorded on a Macintosh 512 computer using the MacTerminal™ program. The data was then converted onto a spreadsheet

program, Microsoft Excel™, versions 2.2 and 3.0. The list of values was cleaned (frequently the second, third, and/or fourth values were less than the normal signal result, or the first was an overshoot, or there was electronic noise which affected the AAS as it was not on a surge protector. These values were deleted as these phenomena are characteristic of signal peaks formed by PE AASs and most other AASs) and the number of readings per volumetric flask for each metal was entered in an adjacent column to the remaining raw readings. Next two specially-developed Excel macros were run on the data. The first macro calculated the mean reading and standard deviation for each metal in each volumetric flask and for each blank and acid blank measured. The second removed the raw values from the data set (copies of all values have been retained on floppy disks). The resulting mean readings were used, along with SA corrections and the adjusted dry weights for each extraction, to calculate the actual sedimentary concentrations using the method of Standard Additions.

In addition to each trace metal mean concentration file, a general file for each AAS run was constructed using Excel. These general files consisted of three columns in the same sequence as the volumetric flasks were. These columns were the flask identification, the level of standard addition present in that flask, and the dilution, if any, in ml for that flask.

2. Computation of Trace Metal Concentrations

The method of Standard Additions was written up as a original Microsoft QuickBASIC program, entitled Absorbance3, for use in this research (A program listing is available upon request).

Typically volumetric flask errors were found after the initial calculation of the mean sediment concentrations and statistical analysis of residuals was necessary to determine in which volumetrics the errors were. The latter process was not automated because results from the BASIC program for the determination of sample concentrations (vs. mean absorbance readings) could not be saved into a file that can be read by other software. As a consequence, the sample concentrations were re-entered into either Excel or directly into a statistics program, Statview™, before the analysis of residuals was performed. Usually not all of the extractions required this analysis, but frequently

most or all of the metals for a given treatment had problems. The common data errors found were that the sedimentary concentrations were negative, the standard deviations were extremely large, or the slopes were very different from the rest of the run for that metal or they differed with respect to typical treatment results. These errors usually meant that one or more of the volumetric flasks within the extraction treatment was either contaminated or the amount of standard addition was incorrect. Once the analysis of residuals had been performed, then the suspect flask(s) could be identified, and the sample was either dropped from further analysis or a correction was made to it, if determinable and quantifiable. Otherwise, the sample value was retained in the set and the datum was treated as if it was a normal outlier.

On a number of occasions during the initial phases of data reduction of the mean trace metal absorbances from the AAS runs, the mean volumetric flask concentrations for two trace metals, zinc and manganese, exceeded the linear range for the primary AAS wavelengths of these metals (concentrations of slightly greater than 1 ppm Zn and over 2.5 ppm Mn). None of the remaining five trace metals ever had this problem. While a second, less sensitive, wavelength exists for high concentrations of manganese and which was used after the first few AAS runs; no secondary wavelength exists for zinc. As a result, occasionally dissolved Zn concentrations in excess of 1.0 ppm were found from time to time throughout this research. Although frequently high Zn concentrations are caused by contamination; for the most part, the observed values did not appear to be due to this problem as both iron and manganese also tended to be high for those extractions where zinc was high and independent evidence supported the presence of high iron in several of the lakes where this phenomenon occurred. Consequently, a method was developed to handle these high Zn (and initially, Mn) concentrations.

Absorbances above the linear ranges for AAS analyses are depressed, so yield lower concentrations than actually present (Perkin-Elmer 1976). This problem was corrected for by routinely including standards greater than the highest unknown found in these analyses. The procedure used was (after subtracting the distilled water blank) to construct a regression equation using all data from standards within the linear range, then to plot this slope and the mean absorbances from all standards measured from above the range of

linearity. Next, a French curve was used to plot the estimated observable concentrations between the known non-linear absorbances and the linear slope. An estimated correction factor was then determined at a number of points within the range of unknowns (= predicted linear absorbance/estimated observable absorbance). These correction factors were then fitted to a linear regression, using the estimated observed absorbance as the independent variable. The percent of explained data for these regressions varied between 92 and 99%. The resultant equation was then used to calculate a predicted absorbance, had the range of linearity extended upwards to include the concentrations of the unknowns. This manipulation freed the subsequently used standard additions technique from the problem of non-linear absorbances caused by high metal concentrations.

3. Statistical Treatment

a. General Procedures

Statistical analyses were performed initially upon a Macintosh SE using the following statistical software: StatView, MacSpin 3.01, and a non-FPU version of Systat 5.1. All initial graphical and cluster analyses were done using these programs on this computer. Due to the slow speed of this machine at the cluster analyses (four in two weeks time of constant 24 hrs $\cdot$ day⁻¹ processing), the computer was upgraded to a Macintosh LC III with a FPU co-processor which yielded over a six-fold increase in the speed of non-mathematical processing alone. The StatView program was also upgraded at this time to version 4.01, using a FPU, and the Systat package was replaced by SPSS 4.0 which could do more of the techniques of interest. The remaining statistical analyses were done mainly using SPSS. Neither SPSS nor Systat had good graphical modules, so all graphics were done by either StatView or by Delta Graph 2.0, used for the fourth quadrant plots only. The maps were hand drawn.

Cluster analyses were used for two purposes, to determine the relationships of summer phytoplankton by lake and sedimentary diatoms by individual core-depth sample, and to determine distributional clusters of phytoplankton and sedimentary diatom species. The objective of the second purpose was to reduce the number of species, or species groups which needed to be analyzed in the next phase of the study. Several different methods were tried during the

first objective; only the Ward minimum variance method using a one-gamma coefficient distance metric gave clear dendrograms which could be analyzed for biological significance while the other methods produced patterns similar to the results of the species cluster analyses, i.e., the same single case, orderly sequential peeling-off noted for the species clusters described below.

No species clusters were found; the analyses always sequentially split off of the main cluster the species farthest away from the centroid. The same order of species was observed whether it was for five clusters or 35. As this set of analyses produced nothing of value, its results were not included here nor analyzed further, and a different procedure for species selection, based upon their relative abundance and broadness of distribution, was used instead.

The species selection criteria were as follows: As very rare species have been demonstrated to bias multivariate statistics (Gauch 1982), these species were removed before the analyses. Very rare species were defined as occurring less than six times among the sedimentary diatoms or less than three times among the summer phytoplankton. These species were retained if their abundance exceeded 1% of any sedimentary diatom sample or 5% of the summer phytoplankton of any lake. A second criterion was derived from the fact that some species were found in only one or two lakes, thus despite high abundances in those lakes, very little could be determined about the trace metal response of these species, except in the case of Oswego where it could be assumed that the species present were tolerant of high Cu concentrations. All other species analyses required a minimum of being present in three study lakes before inclusion.

Trace metals were studied by partial correlation and principle component analyses to examine the role of other water chemistry parameters upon them. ANOVA and Scheffe's Procedure at several levels of statistical significance were used for each extraction to determine whether or not there were any significant differences by both lake class and ecoregion and to identify which pairs of means contributed to the significant F-test result of the ANOVAs.

The majority of the statistical analyses run were stepwise multiple linear regressions (MLR) for reasons to be explained in the following section. The variables used in the MLRs for each biological taxon analyzed included the 22 different trace metal extractions (sedimentary Fe, Mn, Zn, Cu, Co, Ni, and V in

the exchangeable, organic and total available forms plus water column Mo), the seven conservative water chemistry parameters (Na, K, Ca, Mg, Cl, SO₄, and alkalinity), total dissolved summer phosphorus, and the mean trophic status index, plus, depending upon the version of the MLR, summer chlorophyll *a*, Secchi Disk depth, and all ratios between the different trace metals in both the exchangeable and organic extractions as well as, in one set of MLRs only, an estimator of the influence of the redox potential upon each extraction based upon the ratio between each extraction and the total available iron (this last set was a null, so was not further reported on). No analyses were made involving residual metals other than simple descriptive comparisons of their distribution by lake. (Although this seems like a very straightforward task, it generated over 7000 pages of computer printout of data that was worth examining off-screen. Interpretation of this volume has been limited by necessity and only the more interesting results were examined in any detail.)

SPSS can handle over 100 different independent variables at a time and runs stepwise MLRs much faster than StatView (SV) does on the same machine, so it was the principal statistical package used during this phase of the analysis. However, because SPSS can only remove data points from the complete set based upon a single factor, the slower and less capable StatView was used more during the residual analysis.

The different uses of these two software programs can best be illustrated by example (this is a composite sample, not one of any specific species, but it is representative of the type of problem observed on a number of occasions and the specific trace metal-lake combination produced this result nearly a dozen times). The initial results for a species might suggest that the ratio of organic copper to iron was the best factor for predicting the abundance of a particular species of phytoplankton where it occur. However, the SV graph showed that this relationship was based upon the high organic Cu concentrations in Lake Oswego and that without Lake Oswego in the equation, the unadjusted coefficient of determination dropped from over 30% to less than 0.5% (and it was frequently orders of magnitude worse). The SPSS MLR model could not both exclude all null values for this species and the Lake Oswego organic Cu ratios at the same time without a new data set either being constructed from scratch or from editing an Excel data table. SPSS could exclude the null

values and the organic Cu ratios from all lakes could be dropped simultaneously, but since it could not adequately handle missing data simultaneously with case exclusion, that meant that any interactions associated with organic Cu and other trace metals in that extractions for the remaining 20 lakes could not be analyzed. StatView, however, allowed deletion of individual biasing cases, although it could not handle as many different independent variables (on a Macintosh LC with 8 MBs of RAM, the maximum was 37). It was faster to make four to eight MLR runs on a particular species using different, but overlapping, sets of independent variables in SV than it was to re-do the data set for SPSS.

b. Development of the Statistical Approach Used to Determine the Main Trace Metal(s)-Species Interaction(s)

Multivariate statistical methods were originally considered for use in these analyses, but were subsequently rejected. The data sets used in this dissertation represent multiple independent variables and algal species. The algae are distributed in an independent fashion with respect to each other along different environmental gradients. Their distribution may be controlled by one or more of the measured variables. Initially it appeared that these data sets were ideal for a multivariate statistical approach, particularly the group of techniques known as direct gradient analyses, because this type of data is ideal for a Whittaker-style community ecological analysis (Whittaker 1956, 1962, 1967, 1978b, Gauch 1982). However, two conceptual problems arose which dissuaded this approach. First, the objective of this research was to find differences in individual species reactions to individual trace metals or metal ratios, i.e., finding an overriding ecological community phenomenon was not the goal; learning the differences between a number of different species contrasted to each other was. Thus, the results of a multivariate method such as principal component analysis (PCA) would only describe the predominant independent variable(s) influencing most of the species present, not the situation for a single particular species. The primary objective was to find controlling variables for each species and to determine whether or not these sets of variables were uniquely different between species. Another reservation with using a multivariate approach was the inability of the commonly available multivariate

methods (i.e., in commercial statistical software programs) to handle nonlinear data. PCA, a statistical method very widely used by ecologists for the analysis of samples along unclearly understood environmental gradients, is completely unable "to properly handle nonlinear species response curves (Gauch 1982, p. 140)." Since numerous nonlinear trace metal-species interactions were known to be present, PCA was not utilized here. Although the data could be transformed, another problem prevented selection of PCA, the probable presence of Gaussian distributions. Gaussian distributions, which are bivariate instead of univariate in nature, require multiple transformations before use but the sheer volume of untransformed results precluded any use of transformations in the initial analyses.

[As a footnote to this decision, despite the fact that my goal was not to describe the predominant trace metal influences upon phytoplankton and epibenthic diatoms in my study lakes, I was still curious as to what it (or they) might be. Gauch (1982) presented two other direct gradient multivariate techniques, reciprocal averaging (RA) and detrended correspondence analysis (DCA), which could have been used to determine the possible solution. Unfortunately, RA possessed similar problems to PCA. First, secondary gradients do not appear until the third eigenvalue axis due to the fact that frequently the second axis is "merely a quadratic distortion of the first axis. ... The interpretation of results is thus made more difficult because spurious axes must be distinguished from valid axes (Gauch 1982, p.149)." The second problem with RA is that the ends of the primary axis are compressed relative to the axis middle so that a given distance between samples lacks biological constancy. DCA corrected these problems, but was not available in commercial software programs. Consequently, I did not attempt to determine which trace metal(s) was (or were) the predominant factor(s).]

In the subsequent statistical approach used, one aspect from multivariate analyses as applied to ecological questions was retained. This was the concept that the distribution of biological species along direct environmental gradients is actually influenced by only a relatively small number of parameters (Whittaker 1967). These parameters probably include most of the primary limiting factors such as major nutrient concentrations, grazing pressure, light intensity and temperature. However, since studying the effects of such factors on the

abundance and distribution of phytoplankton and epibenthic diatoms was not the main objective of this research, this meant that important parameters were excluded from the analyses. Therefore, evaluations were restricted to considering only the single most important trace metal concentration or trace metal ratio for a given species with few exceptions. This restriction was imposed to limit the inclusion of possibly spurious relationships.

After a review of available statistical procedures, the following approach was selected for the analysis of the species data: First, since the objective was to determine what caused the distribution of individual species, univariate stepwise multiple linear regression (MLR) was probably the best statistical procedure to use. Second, because the concentration of a single trace metal or metal ratio is probably not the primary limiting factor for any species, acceptance of trace metal parameters found during the MLR analyses was restricted to the most strongly correlated one, i.e., the “primary trace metal or ratio” (with a few exceptions which were logically related to each other and/or the primary one). Third, data transformations were limited to situations involving absolute concentrations and to where a graphical display of the data supported such a transformation. The technique of data transformations was later dropped altogether as early analysis suggested that determination of numerical coefficients was an artificial effort at precision which was not supported by the kind of indirect independent variables being examining here. The use of the word “indirect” here is meant to indicate that sedimentary trace metal concentrations do not, of themselves, actually control phytoplankton species composition in the water column. Rather, they are the averaged outcome of interactions between the trace metals themselves with phytoplankton and other substances in the water column. Thus even the primary trace metal parameter found by MLR is actually only the strongest correlation between a sedimentary trace metal concentration or trace metal ratio and the average summer population densities of a given species of algae or cyanophyte, or between trace metals and the relative abundance of diatoms in the sediments at the same depth of deposition. If any causality exists between trace metals and phytoplankton species or sedimentary diatom remains, it is probably only between the mean epilimnetic filterable concentration(s) of the trace metal(s) during the growing season for the particular species under

investigation such as that found by Reynolds and Hamilton-Taylor (1992) for zinc and *Asterionella formosa* in Windermere.

To summarize, MLR was used to find the most strongly correlated trace metal to each species being studied and to get an idea as to the nature of the relationship, i.e., was it directly positive or negative, or did the relationship exhibit a nonlinear pattern; nothing more. Furthermore, when only trace metal ratios were examined, no attempt was made to assess whether or not the relationship was positive or negative as just flipping the numerator with the denominator usually changed the direction of the relationship.

III. Results

A. Vertical Profiles of, and Fractionated Iron Concentrations in, the Collected Cores

1. General Observations

A number of gross morphological features were observed in the cores of the different lakes sampled. While these features were not systematically analyzed, all of the more intriguing ones were catalogued.

The typical sediment core was composed of a uniform, visually featureless, dark gray to brown clay gyttja. Commonly observed exceptions to this pattern included pale colored cores, red iron oxide deposits on the surface of the core liner, sand strata, and volcanic ash and tephra deposits. In terms of color there was a continuum from cream colored to a slate-gray gyttja. Much of the color variability correlated with the amount and type of iron present in the cores. The pattern observed was the darker the color, the higher the amount of iron in the oxide fraction. Deposits of red to orange iron oxide on the surface of the core liners, and inward as much as 2 to 3 mm from the liner, were generally associated with high concentrations of exchangeable iron in the cores. The average concentrations for exchangeable and total available Fe from all lakes are given in Table 3.

Except for the first core analyzed (Carter Lake #1), there were only three depths measured with atomic absorption spectrophotometry (AAS), 2, 5, and 20 cm below the surface. Significant vertical differences were seldom found at this level of differentiation. The four coastal lakes measured by INAA for total trace metal concentrations had more depths measured, hence a number of differences were observed in those lakes.

There were important differences between and within lakes for the percent dry weight, organics, and carbonates in the sediments. Table 4 presents the mean dry weight, percent loss on ignition at 550 °C (i.e., organic material by percent dry weight), and the average percent loss on ignition at 950 °C (or carbonate by percent ash weight; the concentration of carbonate by percent dry weight was carbonate by percent ash weight * [1 - the loss on ignition at 550 °C]) for all lakes.

Table 3. Mean exchangeable and total available sedimentary iron (N=3 per core, 6 per lake)

	FeEx (ppm)	FeTA (%)
A. Coastal ecoregion		
Woahink mid-lake	3680±256	4.49±0.24
St.2	927±91	2.46±0.56
Eel	5400±1410	5.03±0.75
Mercer	4760±1470	6.25±1.58
Carter	30±10	0.46±0.13
South basin		
St. 2 < 6 cm	3360±522	1.69±0.52
> 10 cm	486	0.66
Loon	2920±482	5.86±0.90
Triangle	5590±719	5.94±0.99
B. Willamette ecoregion		
Clear, Marion Co.	436±242	3.53±0.36
Oswego	1980±469	5.63±0.76
C. Cascades ecoregion		
Big deep St., normal	464±147	1.43±0.35 (N=12)
dried & cooked	312±63	
St. 2 (also d&c)	103±42	1.60±0.18
Blue	48±15	0.27±0.19
Suttle	219±125	0.13±0.05
"cooked"	65±35	0.10±0.04
Lava	181±32	0.05±0.01
Todd	8270±803	10.79±1.15
L. of the Woods	71±1	1.74±0.19
Crater South Basin	160±117	2.55±0.04
Wizard Is. Shelf	133±58	2.70±0.11
D. Eastern Transition ecoregion		
East	67±22	1.03±0.23
Paulina	69±21	8.64±1.69
South Twin	192±56	0.47±0.08
E. Blue Mountain ecoregion		
Walton	185±161	2.19±0.60
Morgan	79±20	3.00±0.43
F. Klamath-Siskiyou ecoregion		
Squaw	111±15	6.66±1.26

Table 4. Percent dry weight, organic material and carbonate in lake sediments.

Lake	Dry weight (N)	% Organic (N)	%Carbonate(N)
A. Coastal ecoregion			
Woahink mid-lake	21.2±2.2 (7)	21.1±1.2 (5)	4.0±2.7 (2)
St. 2	26.8±5.7 (6)	11.9±2.9 (5)	3.1±2.3 (2)
Eel	17.4±1.2 (11)	28.1±1.5 (6)	7.0±0.3 (2)
Mercer		21.8±0.8 (5)	9.4±0.2 (2)
#3	15.6±1.1 (6)		
#4	13.5±1.8 (6)		
Carter S. basin	80.5±3.2 (6)	1.5±0.8 (8)	0.6±0.2 (2)
St. 2		15.0±10.3 (4)	1.1 (1)
above 6 cm	22.8±5.3 (3)		
>10 cm	70.5±4.3 (3)		
Loon	43.4±3.4 (12)	12.2±1.9 (6)	6.0±1.0 (2)
Triangle	40.1±7.6 (13)	17.9±1.8 (6)	5.1±0.5 (2)
B. Willamette ecoregion			
Clear, Marion Co.	29.9±6.2 (12)	12.6±1.3 (15)	7.0±1.2 (4)
Oswego	18.9±4.5 (12)	13.8±1.2 (8)	4.2±0.7 (2)
C. Cascades ecoregion			
Big deep St.	11.1±2.0 (10)	31.6±5.8 (16)	6.8±2.5 (4)
St. 2	Not Determined	3.2±0.3 (4)	0.0 (1)
Blue	12.9±1.6 (14)	13.3±1.2 (8)	4.3±0.6 (2)
Suttle	9.2±1.3 (12)	13.4±1.4 (11)	9.0±1.3 (2)
"cooked"	10.4±2.1 (6)		
Lava	6.8±1.0 (14)	15.8±0.9 (6)	15.4±0.2 (2)
Todd	7.3±1.2 (12)	29.3±1.3 (6)	9.5±0.2 (2)
L. of the Woods	12.0±2.5 (10)	24.6±1.1 (4)	7.9±0.3 (2)
Crater			5.2±0.0 (2)
S. Basin	39.4±11.6 (5)	8.7±1.2 (3)	
Wizard Is.Shelf	30.4±1.1 (5)	6.5±1.3 (3)	
D. Eastern Transition ecoregion			
East	11.8±2.1 (9)	20.9±1.5 (6)	14.0±0.1 (2)
Paulina	15.4±3.1 (10)	13.4±2.7 (6)	12.6±3.7 (2)
South Twin	6.1±0.9 (11)	53.3±5.2 (6)	6.2±0.2 (2)
E. Blue Mountains ecoregion			
Walton		25.2±2.7 (5)	7.2±0.3 (2)
#3	13.1±0.9 (6)		
#4	23.8±2.2 (5)		
Morgan	27.4±7.5 (9)	12.2±2.1 (6)	8.7±1.4 (2)
F. Klamath-Siskiyou ecoregion			
Squaw	51.2± 5.4 (11)	9.4±1.7 (6)	7.0±0.1 (2)

2. Lakes of the Coastal ecoregion

Woahink sediments were typically dark gray to brown gyttja with only three features of note. The floc layer was plain brown and quite loose; there was a large amount of sand in the core below the floc layer down to 10 cm, especially in the second core between 2 and 5 cm; and there was iron oxide deposited on the liner from 3 cm downward to 30 cm. The two Woahink cores analyzed for sequentially fractionated trace metals were collected on 9 September 1989, and by 30 November, when they were transferred between refrigerated storage rooms, red iron oxide deposits were already visible, only 82 days after collection. The exchangeable Fe values were typically >1000 ppm (Table 3).

The total trace metal concentrations in Woahink Lake as measured by neutron activation analysis (INAA) were lowest at 4 and 10 cm for the northeast bay core and at 2 cm for the mid-lake core (Figures 8 and 9). Concentrations by depth for Fe, Mn, Co, V, Mo, As, Se, Sb, Br, and Al from Woahink (as well as from Eel, Munsel, and Olalla) Lake(s) are included in Appendix D. Total V from the mid-lake station demonstrated an increase in concentration with decreasing depth, beginning at 10 cm (Figure 9). There was a lack of agreement between the AAS and INAA results for both Woahink and Eel Lakes (Table 5).

Eel Lake sediments were an almost black gyttja below 3 cm with a “rust” coating beginning at the same depth associated with a mean exchangeable Fe concentration of 5400 ppm (Table 3). The sediments of these cores smelled of hydrogen sulfide and numerous small twigs were observed in the sediments as was some sand. Below 2 cm the percent dry weight was very consistent between 15.4 and 19.9% with an average of 17.4% (Table 4). The vertical profiles for total Fe and V did not demonstrate as much vertical differences as those of Woahink Lake (Figures 10 and 11).

The two **Mercer Lake** cores were similar to the mid-lake Woahink core, except there were only small amounts of sand present near the surface of the two cores. The iron oxide deposits on the core liners had not occurred by 30 November 1989 though the cores had been collected on the same day as the Woahink, Eel, and Loon cores. By 1 June 1990 however, half a year later, the red “rust” layer was present along the sides of the core and there was a 1.5 cm thick band of “rust” across the top of the cores. A small quantity of magnetite

Figure 8. Vertical profile of Fe in Woahink Lake sediments.

Figure 9. Vertical profile of V in Woahink Lake sediments.

Table 5. Total trace metal concentrations at 5 cm as determined by AAS and INAA for Woahink and Eel.

	AAS	INAA
Fe (%)		
Woahink mid-lake	5.3	7.3±0.04
northeast arm	2.5	1.6±0.02
Eel	5.6±0.50	6.9±0.19
Mn(ppm)		
Woahink mid-lake	635	383±0.8
northeast arm	467	424±1.0
Eel	481±64	736±50
Co (ppm)		
Woahink mid-lake	81.8	9.3±0.1
northeast arm	44.5	23.6±0.2
Eel	60.7±0.4	16.8±0.4
V (ppm)		
Woahink mid-lake	148	98±4.7
northeast arm	102	27±2.8
Eel	208±13.2	129±4.0

Figure 10. Vertical profile of Fe in Eel Lake sediments.

Figure 11. Vertical profile of V in Eel Lake sediments.

was also observed. The average amount of exchangeable iron for the two cores was 4760 ppm (Table 3). Mercer Lake core #4 was observed in the field to have been less firm than the others collected from this lake and it had a lower percent dry weight than did core #3 (Table 4). The percent of carbonate in this lake was rather high; only five lakes in this study had concentrations similar to or higher than Mercer; Suttle, Todd, Lava, East, and Paulina Lakes (Table 4).

Three cores from **Carter Lake** were analyzed in this study, two from the south basin of the lake and one from farther north in the narrow middle. The first core was dried before AAS analysis. A large part of the Carter Lake sediments appeared to be quartz blown in from the adjacent sand dune. The dried sediment sections from the southern basin cores were mainly gray sand and twigs with no cohesion with very low amounts of organic material and carbonate present, especially in the southern cores (Table 4). The organic material included undecomposed bark and needle fragments. The Carter Lake core liners had thin "rust" coatings at varied depths through the length of the cores. Magnetite was also present in all samples analyzed. The exchangeable fraction for core #3 was humic brown in color, unlike most of the samples collected during this extraction. The average amount of exchangeable Fe for the two southern cores was only 30 ppm (Table 3).

Loon Lake resembled Mercer Lake in nearly all particulars, including a late development of a "rust" coating on the liner, except that the surface layer of iron oxide, at the sediment-water interface, was only 0.2 to 0.3 cm thick. There was an average of 2920 ppm of exchangeable Fe and 5.86% of total available Fe present (Table 3).

Triangle Lake in the Coast Range had typical dark gray gyttja sediments except for the floc layer and top 2 cm which were a red "rust" color. There was a slight sulfide smell from below 50 cm. These sediments were very "stiff" and had a relatively low water content (>40% by dry weight) and an average total available Fe near 5.9% like the sediments of Loon Lake. The thickness of the "rust" coating, though present, was not recorded.

Total sedimentary trace metal concentrations of both Olalla Reservoir and **Munsel Lake** were also measured by neutron activation. Unfortunately neither lake were analyzed by AAS, nor were the sediments generally characterized. The vertical profiles for the INAA concentrations of Fe and V for

Munsel Lake are plotted in Figures 12 and 13. Like in Eel Lake these profiles did not demonstrate much vertical difference as opposed to those of Woahink Lake.

Cores from Clear Lake, Lane Co., were also collected, though not analyzed by AAS or INAA. However, the entire 78 cm length of one core was visually examined. This core was dark gray gyttja, having a distinctly sandy texture with a 2-3 mm thick “rust” layer lining the outside of the core and possessing a faint odor of H₂S, much like the Carter, Woahink, and Mercer cores. All of the cores from Coastal lakes with “rust” coats on the liners had exchangeable Fe concentrations near to or greater than 1000 ppm (Table 3), so it is probable that the exchangeable Fe concentration in this lake was also greater than 1000 ppm.

3. Lakes of the Willamette ecoregion

Three cores from **Clear Lake**, Marion Co., were analyzed. All three were unremarkable gray gyttja cores with a small quantity of magnetite present. Core #1 was dried before analysis and had significantly lower concentrations of Fe and higher concentrations of Zn present than did the other two.

Two cores were analyzed of six collected from **Lake Oswego**. Oswego sediments were dark gray gyttja with “rust” on the core liner along most of their length and gas bubbles between 8 and 22 cm. Magnetite was observed and a slight “sewer” odor noticed at 5 and 20 cm of the second 1988 core. Again with a “rusty” core liner, the mean exchangeable Fe concentration was over 1000 ppm (Table 3). The Oswego sediments had a relatively low amount of carbonate for lakes in this study as the only lower ones were Carter and Woahink (Table 4).

Mission Lake (Marion Co.) sediments, otherwise not analyzed, had a mixed clay, sand, and gravel structure. The lake is less than 100 m from the Willamette River and apparently is a very recent oxbow as the gravel is only 2 to 4 cm below the surface of the sediments.

4. Lakes of the Cascade ecoregion

Five cores from **Big Lake** were analyzed. Cores #1 through #3 were cooked and both cores #1 and #3 were dried before analysis as well. Core #3

Figure 12. Vertical profile of Fe in Munsel Lake sediments.

Figure 13. Vertical profile of V in Munsel Lake sediments.

was from the second station at the north end of the lake (Figure 4) while the other four cores were from the deeper station. Cores #4 and #5 were mostly dark gray-brown gyttja with some magnetite present. Core #5 had a more reddish cast to it between 15 and 30 cm than either above or below. Core #3 was sandier between 12 and 36 cm than were #2, #4 and #5 and had more magnetite present. The concentration of exchangeable Fe was statistically significantly lower at the deep station than at the north station (Table 3). However, the total available iron did not differ between the cores (Table 3).

Blue Lake in the Santiam Pass had sediments which were a pale yellowish cream color when wet and which dried to a pale blue-gray. The sediments of core #5 were 80 to 90% diatoms by volume. Three gray ash-like bands were observed in the first three cores; the shallowest one was about 46.5 cm below the sediment-water interface. Both exchangeable and total available Fe in Blue Lake were relatively low for the study lakes (Table 3). Suttle and Lava were the only lakes with lower concentrations of total available Fe, while South Twin and Carter Lakes had similar concentrations. Carter, East, Paulina, and Morgan had similar concentrations of exchangeable Fe to Blue Lake; Squaw, Suttle, Crater and Lake of the Woods had slightly higher concentrations.

Three cores were examined from **Suttle Lake**. One, #1, was cooked before analysis. The cores were a pale tan, slightly darker than Blue Lake. The cores dried to the same pale blue-gray color found in Blue Lake. They similarly had a low average dry weight (Table 4) and total available Fe (Table 5).

Lava Lake sediments were runny and pale olive to khaki colored. Dried sediments were similar in color and composition to those of both Blue and Suttle Lakes (Tables 3 and 4).

Sediments from **Todd Lake** were a dark, humic brown in color. An apparent ash layer was observed between 7.5 and 7.7 cm below the sediment-water interface, and there was an orange to khaki-colored deposit on the core liner. The average concentration of iron was relatively high (Table 3). However, the sediments were rather soft and watery (Table 4), hence the amount of iron deposited per unit of sediment volume was smaller than these values suggest.

Lake of the Woods had runny, light brown sediments. The sediments were similar to those of Blue and Suttle, except for a higher concentration of

organic material and a greater amount of FeTA (Tables 3 and 4), hence were darker.

The two cores from **Crater Lake** were taken from two different locations, in the deep southern basin and on the Wizard Island shelf (Figure 6). The south core, taken in August 1989, came from a depth of 530 m; while the shelf core was from “only” 274 m. This core was collected a year earlier than the deep core. The deep core was stiff, relatively coarse-grained, and a medium orange-brown in color; the shelf core was finer-grained and paler in color, but otherwise had a similar structure. Magnetite was present in both. The sediments overall dried to a pale gray in color, though there was also a pale orange color in parts of the South Basin core as well as on the top of the Wizard Island core. There was no difference in mean exchangeable or total available Fe concentrations between the two cores (Table 3). However there was a significant depth difference in exchangeable Fe concentration; at 5 and 20 cm the mean concentration was 181 ± 83 ppm, while at 2 cm it was only 77 ± 3 ppm.

5. Lakes of the Eastern Transition ecoregion

The sediments of **East Lake** were an olive drab color which quickly dried to a pale tan without any “rust” on the core liners and which lacked a hydrogen sulfide smell despite the presence of sulfur springs near the southeast shoreline of the lake. No magnetite was observed. **Paulina Lake** sediments were a darker olive drab color than those of East Lake and there was a detectable faint sulfide smell in the floc layer unlike in East Lake. Below 5 cm within a span of a cm or so, the color changed from a brownish tone to very dark gray, or almost black, with a turquoise cast to it. The only difference between the two cores collected from this lake was a more yellowish floc layer in the second one analyzed. Sediments in Paulina Lake had a slightly higher dry weight than those of East Lake, and there was significantly less organic material present (Table 4). The most notable features about the Fe fractions in the sediments of these two lakes were the significantly larger amount of total available in Paulina (Table 3) and the increased concentration of exchangeable at 20 cm in East over the shallower depths (an average of 93 ± 12 vs. 54 ± 7 for 2 and 5 cm).

Sediments from **South Twin Lake** were very loose and runny as the percent dry weight below 2 cm was only 6.1% (Table 4). Over half of the dry

weight was organic material (Table 4). The South Twin sediments resembled those of Lava more than those of the Newberry lakes (Table 3 and 4), except for the uniquely high percentage of organic material. The composition of the organic material was not readily apparent as there were no twigs or conifer needles visible nor was it composed of diatoms. Two ash layers were found deep in the first two cores from this lake as well as in the adjacent North Twin Lake (at 55 and 75 cm). Overall the sediments were a chocolate brown in color with very small amounts of magnetite observed.

6. Lakes of the Blue Mountains ecoregion

True sediments in **Walton Lake** were only 6-7 cm deep, however the soil at 20 cm was chemically quite similar to the overlying sediments. Except for a net of root hairs just below 5 cm, the texture was essentially a fine ooze for core #3 and Core #4 was a somewhat stiffer ooze. While the two cores had different mean dry weights (Table 4), there was little difference between depth in either. Except for the plant roots at 5 cm in #3, the percent organic material was also quite uniform. The color of these cores was a medium brown to a dark humic brown. In the fifteen months between their collection in August 1989 and their analysis in November 1990, both cores developed an iron oxide precipitate on the core liner and some magnetite was observed in them. Exchangeable Fe averaged only 185 ppm however (Table 3), but there was a significantly more FeEx at 20 cm in the soil zone than at 2 and 5 cm (386 ± 73 vs. 85 ± 28 ppm) .

Morgan Lake sediments were a dark brown, thick sticky gyttja with some magnetite present, but almost no floc. Iron concentrations were similar to Walton's, but Morgan had only about half the amount of organic material (Table 4).

7. Lakes of the Klamath-Siskiyou Mountains ecoregion

Sediments from **Squaw Lake** were a dark gray gyttja which had a strong "soapy" texture to them, like a thick, very greasy, clay. The sediments were stiff and very firm with a high mean dry weight (Table 4). Below 40 cm, the sediments were black (FeS?) and softer, and there were small amounts of sand throughout the cores. There was little organic material present (Table 4); only

Crater Lake, the southern basin of Carter Lake, and the shallow water station in Big Lake had lower concentrations. During the HCl extraction Squaw Lake sediments developed a unique lustrous silver color, possibly due to some form of zinc. Total available Zn averaged 138 ppm; only Clear Lake and Lake Oswego had higher Zn concentrations among the study lakes.

B. Sedimentary Trace Metal Concentrations Other than Exchangeable and Total Available Iron

Final sedimentary trace metal concentrations, including all forms of iron, for all lakes and sediment depths are presented in Appendix A.

1. Peroxide-extracted iron concentrations

Peroxide-extractable organic and sulfidic iron varied greatly from lake to lake in this study as well as within the sediments of a number of lakes. With the exception of the Newberry Caldera lakes where sulfur springs are present, this fraction was always the smallest of the three iron components analyzed for at all depths. East Lake #3 had the highest amount of peroxide-extracted iron, an average of 4985 ppm; East Lake #4, and Todd #3 and #4 were the only other cores with average peroxide-extracted iron over 1000 ppm. Eel, Mercer, one core from Woahink, Triangle, and Paulina Lakes had values averaging over 100 ppm. Lakes with concentrations at 10 ppm or below included Carter, Oswego, Blue, the deep Crater core, Lake of the Woods, Morgan and Squaw.

2. Sedimentary manganese concentrations

Often the largest component of total available sedimentary manganese in these lakes was the exchangeable fraction. Four of the six coastal lakes had exchangeable Mn concentrations in their sediments of between 250 and 380 ppm. Exchangeable Mn in Triangle Lake was 145 ppm while Carter had an average of about 50 ppm. Oswego had a mean concentration of exchangeable Mn of about 225 ppm; Clear Lake's average was 78 ppm.

The only Cascade and Eastern Transition lakes with exchangeable Mn concentrations greater than 100 ppm were Crater Lake (both stations), the Newberry Caldera lakes, and Todd Lake. Paulina had the most of any lake in this study, averaging about 600 ppm of exchangeable Mn, while East Lake

averaged about 235 ppm, and Todd had between 190 and 240 ppm. The Wizard Island shelf core possessed a mean of 156 ppm but the south basin core had the second highest concentration of exchangeable Mn, 433 ppm.

All three lakes in the Santiam Pass had less exchangeable Mn in their sediments than the lowest value found in the Maritime lakes. The average for Big Lake was 13 ppm and at the north station it was significantly lower, only 5 ppm. Blue Lake had a mean concentration of exchangeable Mn of just under 9 ppm while Suttle averaged slightly over 10.5 ppm. The concentration of exchangeable Mn in Lava Lake was also very low, less than 7.5 ppm. By contrast, both Lake of the Woods and South Twin Lake had mean concentrations near 50 ppm of exchangeable Mn, only a little lower than the Maritime lakes.

These wide regional differences in the concentration of exchangeable Mn were one of the more striking geochemical findings of this research.

With the exception of ten cores, the hot peroxide extraction consistently had the smallest fraction of manganese. The ten exceptions were the Wizard Island shelf core from Crater Lake, the four cores from the Newberry Caldera lakes (this fraction was actually the largest one in East Lake), one core from Lava Lake, and both cores from South Twin and Todd as well as one core from Squaw Lake. (The Wizard Island shelf core is grouped in with this group solely because the 2 cm depth sample has an extremely high concentration of "organic" Mn; it may be more appropriate to treat this single sample either as a separate identity or as an uncorrected error.) With the exceptions of the Lava Lake and South Twin cores (mainly due to extremely low values of the other fractions), all of the high hot peroxide extraction lakes are known, or believed, to have high concentration of sulfides, either in the watershed or the lake itself.

The majority of western Oregon lakes had "organic" Mn measurements between 30 and 110 ppm. Organic Mn was lower in Carter Lake (all samples were below 26 ppm, the mean = 7 ppm) and higher in Lake Oswego (216 ppm).

Lava Lake and the three Santiam Pass lakes had very low concentrations of organic Mn; only a single value of the 36 measured was above 13 ppm (a 19 ppm). The averages for Big, Blue, Suttle and Lava Lakes were 4.0, 1.7, 2.6, and 6.5 ppm, respectively. The north station of Big Lake had a mean concentration of just 0.6 ppm of organic Mn. Lake of the Woods and South Twin Lake were also low, though not as extreme as the previous group. Lake of the Woods

had an average of 10 ppm of organic Mn while South Twin's was just over 22 ppm.

The Crater Lake samples with the exception of the 2 cm depth on the Wizard Island shelf averaged 44 ppm. This was the only Cascade or Eastern Transition Zone ecoregion lake to possess organic Mn concentrations similar to western Oregon lakes.

The highest concentrations of peroxide-extracted Mn among the study lakes were found in Paulina Lake and the second highest, excluding the 2 cm Wizard Island shelf value, occurred in East. Paulina sediments averaged 1890 ppm of organic+sulfidic Mn, while East's mean was nearly 370 ppm. The 2 cm depth of the Wizard Island shelf core produced a reading of 420 ppm. The remaining Cascade lake with high peroxide-extracted Mn was Todd with a mean of 170 ppm.

The amount of manganese in the HCl extraction varied widely between the different lakes studied, but distinctive regional differences were not found. In the lakes of western Oregon the average of the oxyhydroxide+carbonate fraction ranged from 39 ppm in Carter and 66 ppm in Eel to 381 ppm in Oswego and 225 ppm in both Loon and Clear Lakes. In the Cascades and Eastern Transition ecoregions, only Paulina had Mn oxide+ carbonate values over 400 ppm and Blue, Suttle, Lava and South Twin were the only lakes with means under 25 ppm. The Mn oxide+carbonate concentration in Paulina averaged nearly 4800 ppm while the four low lakes averaged 23, 9, 2.2, and 17 ppm, respectively.

The only within-lake differences observed for manganese oxide+ carbonate were a reduction in concentration at 5 cm in the northeast Woahink station, a statistically significant higher concentration at the north station in Big Lake ($160. \pm 4.3$ ppm vs. 44.9 ± 18.3 ppm for the deep station), and a weak differentiation between the South Basin and Wizard Island shelf cores from Crater Lake (the mean concentration was higher in the core from the shelf).

The exchangeable manganese concentrations for the two Blue Mountain lakes sampled were quite variable with individual measurements ranging from 62 to 281 ppm. The mean value for both lakes was slightly over 150 ppm. Similarly, the organic fraction in these two lakes was very variable. Both, however, showed a consistent decline in concentration of the "organic" fraction with

depth. The mean concentration of organic+sulfide Mn was 33 ppm; on the average, Walton had more than Morgan, but the difference was not significant. There was no significant depth changes in manganese oxides in either lake, while the mean concentrations of this fraction, for a change, did differ between them. Morgan had an average of 168 ppm, Walton's was 102 ppm; two Morgan values overlapped three from Walton, the rest were clearly distinct.

The two Squaw Lake cores had distinctly different Mn distributions and concentrations. Core #1 was a "typical" core; exchangeable Mn averaged 204 ppm, the mean peroxide fraction was 57 ppm, and the HCl extraction was 426 ppm, while core #2 had averages of 35 ppm of exchangeable Mn, 650 ppm of peroxide-extracted Mn, and 1032 ppm of HCl-extracted Mn. The first core had greatly elevated concentrations of "organic" and oxides+ carbonates at 2 cm vs. the lower depths sampled while the second core possessed a consistent reduction in concentration with increasing depth for all three extractions.

3. Sedimentary zinc concentrations

Nearly all of the zinc found in this study occurred in the oxide fraction with few exceptions. Zinc in the HCl extraction ranged from 1.5 ppm in Lava Lake and 6.6 ppm in East Lake to 174.6 ppm in Lake Oswego and 178.5 ppm in Lake of the Woods. The mean value for this fraction was 68.3 ± 54.2 ppm. The relative importance of zinc in the other two extractions with respect to the oxide fraction and to each other varied from lake to lake. Zinc in the oxide+carbonate fraction represented between 75% (Eel) and 99% (Loon) of the total available Zn in the sediments of the eight western Oregon lakes studied, and was over 95% of the total available sedimentary Zn from the two Blue Mountain ecoregion lakes. In addition to Lake Oswego, Clear Lake had a HCl-extracted zinc concentration higher than one standard deviation from the mean of all of the study lakes. Carter Lake, at 18.2 ppm of zinc in the oxide+carbonate fraction, possessed the lowest concentration of these ten lakes.

Of the eleven lakes analyzed from the Cascades, Eastern Transition, and Siskiyou ecoregions, seven had concentrations of zinc in the HCl extraction over 65% of the total available from the sediments. In addition to Lake of the Woods, Squaw also had a mean absolute Zn concentration greater than one standard deviation above the mean (135.0 ppm), while Blue Lake had a

significantly lower mean zinc “oxide” concentration (11.8 ppm). Both Big and Blue Lakes had zinc “oxide” concentrations which were 66% of the total available Zn and the equivalent value for Todd was 69%, while Squaw, Paulina, Crater and Lake of the Woods had oxide to total available fractions greater than 90%. The Zn distribution in the sediments of the remaining four lakes, East, Lava, Suttle, and South Twin, varied significantly from the other 17 lakes of this study. Thirty-two percent of the total available sedimentary Zn in East Lake was in the HCl extraction, 54% of South Twin's, 50% of Suttle's, and only 7% (!) of Lava's.

Among the coastal lakes, Coast Range lakes, lakes of the Willamette Valley ecoregion, Squaw Lake, and the lakes from the Blue Mountains, exchangeable Zn averaged at or below 2.5 ppm, except for Mercer (6.3 ppm) and Oswego (4.2 ppm). On the average, concentrations of exchangeable Zn were higher in the lakes of the Cascades and Eastern Transition ecoregions. Only the three caldera lakes and Todd Lake had low exchangeable Zn concentrations, similar to the lakes of the other four ecoregions. East and Paulina Lakes had the lowest concentrations (0.6 and 0.9 ppm, respectively) of all 21 lakes. The highest concentrations of exchangeable Zn (>10.4 ppm) were found in Big (24.1) and Lava (18.5) Lakes. Exchangeable Zn concentrations were 5.5 ppm for Blue Lake, 9.5 ppm for Suttle, 4.2 ppm for Lake of the Woods, and 6.0 ppm for South Twin.

Organic+sulfidic zinc values averaged 6.0 ppm; however, a bimodal distribution pattern is a more accurate way to describe sedimentary Zn from this extraction. Significantly higher than average concentrations (>12.0 ppm) occurred in Eel (19.1), Mercer (14.7), East (13.6), South Twin (12.2), and Todd (14.2) Lakes, and Oswego (11.5) almost fell in this grouping as well. On the other hand, low values for this fraction (<3.0 ppm) were found in Carter (0.6), Woahink (2.4), Loon (0.2), Morgan (0.6), Walton (1.1), Squaw (0.4), Blue (0.6), Lava (0.5), Paulina (1.1), and Crater (1.2) with Triangle (4.0) and Suttle (4.3) just slightly above this range. Only three lakes had “typical” (?) organic Zn concentrations, Clear (7.8), Big (7.2), and Lake of the Woods (7.7).

Two features are worth emphasizing about the distribution of sedimentary Zn. First, despite the overall predominance of the Zn oxide+carbonate fraction, most of the statistically significant correlations between Zn and species of

phytoplankton or sedimentary diatoms were not with this fraction, but were with the exchangeable and "organic" fractions (See Section III.G). Second, even though there were galena crystals on the shore of Squaw Lake, most of the Zn in the sediments of this lake re-distributed into the oxide fraction. Initially, the cause of this re-distribution was believed to be due either to cooking or to a systematic problem with the method of extraction; however, the presence of high "organic" Zn concentrations in lakes which either have known or probable sulfide inputs (East and Todd, respectively) or are anoxic during the summer (South Twin and Oswego) argued against a serious systematic problem with the method of extraction, while moderate concentrations in the dried cores of Triangle and Lake of the Woods combined with no significant differences between Big #1 (dried and cooked), #3 (cooked only), and #4 and 5 suggested that being cooked or dried were not critical factors. The re-distribution of Zn within Squaw Lake sediments appeared to be due to a different mechanism.

4. Sedimentary copper concentrations

Exchangeable copper (CuEx) concentrations in the 21 lakes were very low. The only lake where exchangeable Cu exceeded 10 ppm was Crater Lake (11.7 ppm); the Wizard Island shelf core had the higher average concentration. No other lake mean even exceeded 5 ppm exchangeable Cu. Suttle, Todd, and Squaw were the only lakes with CuEx concentrations greater than 2.5 ppm besides Crater. Both Suttle and Todd had CuEx concentrations of 3.1 ppm while the mean exchangeable Cu concentration for Squaw was 3.4 ppm. The following lakes had less than 1 ppm exchangeable Cu: Carter (0.89), Woahink (0.54), Loon (0.69), East (0.99) [Paulina's was 1.04], Morgan (0.84), and Walton (0.89).

Four lakes had high mean HCl-extracted Cu concentrations, Oswego (230 ppm), Squaw (108), Crater (71.4) and Big (51.2 ppm for the main station only). The two stations in Crater Lake had significantly different concentrations; the south basin core averaged 55.9 ppm while the mean of the Wizard Island shelf core was 86.9 ppm. Lakes with mean Cu concentrations in the oxides+carbonate fraction lower than 10 ppm included Carter (4.21 ppm), Suttle (9.53), Lava (2.47), East (3.80), Paulina (5.76), and South Twin (6.84).

Organic copper concentrations varied by a factor of over 300 fold between Carter Lake (0.22 ppm) and Lake Oswego (69.4). The arithmetic mean was 9.0 ± 14.7 ppm; the geometric mean was 4.25 ppm while the range of one geometric standard deviation was from 1.16 to 15.5 ppm. Three lakes in addition to Carter had concentrations of organic Cu below one geometric standard deviation from the mean, Loon (1.01), Paulina (0.86), and Morgan (1.02). One lake besides Oswego had a concentration of organic Cu greater than one geometric standard deviation above the mean, Crater (16.0 ppm), due solely to the average value of the Wizard Island shelf core (24.7 ppm).

5. Sedimentary cobalt concentrations

Sedimentary cobalt did not vary widely over the range of the study lakes. The range of mean exchangeable Co concentrations was less than 15 ppm, from 1.56 for Carter Lake to 16.4 at the main station of Big Lake. Similarly, cobalt from the peroxide extraction had a narrow range of values from 0.42 for Carter Lake again to 11.3 for Todd Lake. The cobalt associated with oxyhydroxides and carbonates had a somewhat wider range from 1.95 ppm in Blue Lake to 39.6 ppm in Paulina, but the range for cobalt was still narrow when compared to the commoner trace metals in this extraction.

The mean concentration of exchangeable cobalt in the sediments of the study lakes was 7.07 ± 3.96 ppm. In the Maritime lakes of western Oregon, only Carter and Mercer had average concentrations which differed by more than a single standard deviation from the mean. The mean exchangeable Co in Mercer Lake sediments was 13.2 ppm. None of the three lakes in either the Blue or Klamath Mountains had exchangeable Co concentrations which differed from the grand average. In fact Squaw Lake's value of 7.00 ppm made it the closest lake to the overall average. Likewise, the three lakes in the Eastern Transition ecoregion, East, Paulina, and South Twin, were also quite average in their mean exchangeable Co concentrations. Their total range of mean values was only 1 ppm, between 5.86 in East Lake and 6.86 in South Twin.

Most of the variation in exchangeable Co outside of the low value for Carter Lake was found among the lakes of the Cascade ecoregion. Blue Lake had the second lowest mean concentration, 2.06 ppm. This was the only other value which was significantly lower than average) In addition to the deep

station in Big Lake, Suttle, Lava, and Todd all had mean concentrations of exchangeable Co significantly higher than the overall average. The means for these three lakes were 12.2, 11.7, and 13.0 ppm, respectively.

Sedimentary "organic" cobalt had an arithmetic mean of 4.10 ± 3.04 ppm. The geometric grand mean was only 2.93 ppm; however the range for one standard deviation from both means was essentially identical, approximately 1.1 to 7.3 ppm. Six lakes had mean concentrations of peroxide-extracted Co outside of this range, four in the Coastal ecoregion, and two in the Cascades ecoregion. Lakes with low concentrations of "organic" Co were, besides Carter, Loon (0.74 ppm) and Blue (0.57 ppm). The two coastal lakes with higher than average concentrations of peroxide-extracted Co were Eel (7.92 ppm) and Mercer (9.20).

The sedimentary cobalt freed by the hot HCl treatment averaged 17.70 ± 9.60 ppm for the 21 lakes examined in this research. Thirteen of these lakes had means of between 14 and 26 ppm. Only two lakes had significantly higher mean concentrations of cobalt in the oxyhydroxide+carbonate extraction, Paulina and Squaw (39.0 ppm). Carter Lake was the only lake in western Oregon to have low mean concentrations of this fraction (3.58); however, five of the seven lakes sampled in the Cascades ecoregion had low HCl-extracted Co concentrations. Besides Blue Lake, both Big and Suttle had low concentrations of cobalt associated with sedimentary oxides and carbonates, 10.9 and 13.0 ppm, respectively, as did Lava (9.22) and East (4.68). As East and Paulina did not differ at all in either of their other cobalt fractions (exchangeable Co: 5.86 vs. 6.62 ppm and "organic" Co: 6.79 vs. 4.92 ppm), the contrast between these two lakes for this Co extraction was quite stark.

One measurement of cobalt in the oxide+carbonate fraction, Morgan #1 at 20 cm (134 ppm), was quite divergent from the rest of the readings for either that lake or for all of the measurements of this extraction. This value was probably due to a contaminant, so was dropped from the analyses.

When all three extractions of cobalt are summed up as the total available, the mean values for this parameter remained roughly between 20 and 50 ppm with only three noteworthy exceptions, Carter and Blue Lakes at 4.6 ppm and East Lake at 17.3 ppm. The significance of this finding will be discussed further in Section IV.C.2.c.

6. Sedimentary nickel concentrations

While mean exchangeable Ni varied little between the 21 lakes and “organic” nickel was only slightly more variable, Ni in the oxide fraction had a wide range of values. The range of exchangeable Ni was from 1.79 ppm for Carter Lake to 22.1 ppm for the main station of Big Lake. “Organic” Ni went from below the detection limit in Lava Lake and 0.38 ppm in Carter Lake to 19.4 ppm in Todd Lake and 25.4 ppm in Paulina Lake. No nickel was detected in the oxide fraction of Lava Lake, but the same fraction in Squaw Lake averaged 274 ppm.

The grand average for exchangeable Ni was 7.74 ± 5.82 ppm. Only the mean concentration in Carter Lake was more than one standard deviation below the grand average for all of the lakes sampled. South Twin, at 15.4 ppm, and Todd were the only other lakes besides Big Lake to have significantly higher concentrations of exchangeable Ni.

“Organic” nickel had a grand average of 6.89 ± 6.38 ppm; however, most of the “organic” Ni means clustered into several tight groups with a distinctly skewed distribution (Figure 14). The single largest group had mean concentrations between 3 and 4 ppm (8 lakes). Three lakes had average “organic” Ni values below 1 ppm, and another three were between 5 and 6 ppm. The remaining seven lakes, all above 7 ppm, gradually spaced out farther and farther apart. Of the eight lakes sampled from the Maritime area of Oregon, four had “typical” concentrations (i.e. between 3 and 4 ppm), two had less than 1 ppm of “organic” Ni, Carter and Loon, and the remaining two, Eel and Mercer, had concentrations above 7 ppm, 9.67 and 11.5 ppm, respectively. Two of the Blue and Klamath Mountain lakes ecoregions had typical “organic” Ni concentrations, Morgan and Squaw, while Walton averaged 5.36 ppm. The ten lakes of the Cascades and Eastern Transition ecoregions tended toward higher mean concentrations of “organic” Ni than lakes of the other ecoregions. Half of these lakes had mean “organic” Ni concentrations greater than 7 ppm. Todd had the second highest mean (19.4 ppm) after Paulina. Except for Lava, the only lakes with less than 5 ppm of “organic” Ni were Blue (3.04 ppm) and Crater (3.79 ppm). The other two lakes with mean concentrations between 5 and 6 ppm of “organic” Ni were East (5.06 ppm) and Lake of the Woods (5.83 ppm).

Figure 14. Frequency diagram for peroxide-extracted nickel.

The two lakes with the highest amounts of “organic” nickel had also had clear vertical differences in their exchangeable and “organic” Ni. The concentrations of these two fractions were distinctly enriched in Paulina at 2 cm. Todd, on the other hand, had much more of these two fractions at 20 cm than in the shallower depths. These vertical differences, which might be important, were not present in the oxide fraction of nickel.

With three exceptions, mean concentrations of sedimentary nickel in the oxyhydroxide+carbonate extraction (NiOx) were below 50 ppm. The lake with the highest concentration of nickel in this fraction was Squaw at 274 ppm. Paulina (62.4 ppm) and the north station of Big Lake (64.4 ppm) were the other two sites with high NiOx concentrations. The only lake in western Oregon with less than 20 ppm of NiOx was Carter (8.4 ppm). These were several lakes in the Cascades and Eastern Transition ecoregions with sub-20 ppm of NiOx. These included Blue (6.8 ppm), Suttle (12.9), East (4.1), and Todd (15.2) along with Lake of the Woods, South Twin, and the Maritime Woahink at just over 20 ppm (21.0, 21.8, and 20.9, respectively). The lowest amount of nickel observed in the oxide fraction was in Lava Lake where it was below detection limits. The remaining ten lakes had mean NiOx concentrations between 22 and 45 ppm, averaging 31.5 ± 7.0 ppm.

7. Sedimentary vanadium concentrations

The mean concentration of exchangeable vanadium in the sediments of the study lakes was 19.4 ± 15.0 ppm dry weight. However, a better description of it would be by “natural” groupings. The lowest group were five lakes with less than 7 ppm of exchangeable vanadium (VEx). The highest group were those lakes with greater than 40 ppm of VEx, Big (41.2 ppm at the deep station), Lava, (57.5) and Todd (45.1). Four more lakes had mean VEx concentrations between 25 and 31 ppm (Mercer, Suttle, Paulina, and Walton). The remaining nine lakes had mean concentrations of VEx between 9 and 22 ppm. The eight lakes sampled from western Oregon had lower mean VEx concentrations than those of the three eastern mountain ecoregions. Carter and Triangle tied for the lowest value, 2.3 ppm, followed by Loon at 5.4 ppm, while Mercer at 30.0 ppm was the Maritime lake with the highest concentrations of VEx. Eel had

the second highest concentration, 21.1 ppm. Likewise, Squaw in the Siskiyou also had a very low mean concentration of VEx, 2.9 ppm.

The mean concentration of exchangeable V from the 12 lakes from the Cascades, Eastern Transition and Blue Mountain ecoregions was 25.9 ± 15.4 ppm as opposed to an average of 10.8 ± 9.4 ppm from the nine lakes of western and southern Oregon. Lake of the Woods, with 6.4 ppm of VEx, had the lowest mean concentration of this fraction of any of the mountain lakes sampled during this study. East (12.7 ppm), Crater (13.6 ppm), and South Twin (14.2 ppm) were the only other subalpine lakes sampled with less than 15 ppm of VEx.

The variability of "organic" vanadium (VOr) was larger than that of the exchangeable fraction. Three lakes had mean concentrations greater than 100 ppm, Big (108 ppm), Lava (103) and South Twin (137). On the other hand, mean concentrations of VOr was less than 12 ppm for nine lakes, six in western Oregon along with Squaw Lake as well as Crater (4.8 ppm) and Morgan (7.6 ppm). Carter (1.9 ppm) and Squaw (2.7 ppm) had the lowest means; that of Triangle equaled Crater Lake's value. Loon, at 6.0 ppm, was quite low also. Four lakes had VOr concentrations between 19 and 25 ppm, including the remaining two lakes from the Maritime ecoregions, and two more lakes (East and Lake of the Woods) had concentrations between 30 and 35 ppm. The final three lakes, Blue, Suttle, and Todd, had mean VOr concentrations between 50 and 80 ppm. The six lakes with the highest V concentrations from the peroxide treatment usually the greatest concentration at either the 2 or 5 cm depths.

Vanadium in the oxides+carbonate extraction (VOx) did not vary as much as did the previous two fractions. Twelve of the 21 lakes had concentrations between 100 and 200 ppm, while an additional five had concentrations between 35 and 50 ppm. The latter lakes were Woahink (49.4 ppm), Blue (43.1), Suttle (41.4), East (36.9) and Lake of the Woods (45.3). Paulina (74.3 ppm) and Lava (66.6 ppm) had VOx concentrations intermediate to the previous two groups. The two extremes were found in Carter (11.6 ppm) and Todd (329 ppm). The second highest VOx concentration was found in Big Lake at the deep station (175 ppm), while the two lakes from the Willamette Valley ecoregion were the only other lakes with concentrations above 140 ppm.

8. Residuals trace metal concentrations

The mean residual sedimentary concentrations at 5 cm for the seven trace metals are presented in Appendix A. These values primarily represent allotho-nous clastic materials associated with silicates.

Lakes from the maritime areas of western Oregon formed two groups when their residual Fe concentrations were examined. Most of them had residual Fe concentrations between 6000 and 10,000 ppm; however, Carter, Loon, and one of the Triangle Lake cores ranged between 2000 and 4000 ppm.

The montane lakes demonstrated a higher degree of variability in their residual Fe concentrations from less than 400 ppm in Lava Lake to over 30,000 ppm at the north Big Lake station. Big Lake and the Wizard Island shelf core had the highest concentrations, 14,900 and 11,600 ppm, respectively. Lake of the Woods, at 10,300 ppm, was the only other lake with a mean residual Fe concentration above 8000 ppm, though Walton Lake had a single value of 9100 ppm. The core from the south basin of Crater Lake had a value of 7400 ppm. Blue, two of the three Suttle Lake cores, Todd, South Twin, Morgan and the other Walton Lake core had residual Fe concentrations between 2000 and 4000 ppm and Squaw was just over 4000 ppm at 4700. Besides the Lava Lake sediments, the third Suttle Lake core was below 1000 ppm, and the two Newberry Caldera lakes had mean concentrations between 1000 and 2000 ppm.

Residual manganese concentrations in coastal and Coast Range lakes varied from 18 ppm in Loon Lake and 27 ppm from one of the Triangle Lake cores to 80 ppm at the mid-lake station in Woahink. Concentrations of residual Mn were higher in the two Willamette Valley lakes, 107 ppm in Clear and 72 ppm in Oswego. Again the montane lakes revealed a greater variability with Lava the lowest at 8.5 ppm and Big averaging 201 ppm with a concentration of 283 ppm at the north station. Residual Mn concentrations averaged between 25 and 50 for Blue, two of the three Suttle cores, Todd, and Squaw; while it was between 50 and 100 ppm for most of the rest of the lakes sampled. The third Suttle Lake core was the only other core with a value below 20 ppm, while both Crater Lake cores had residual Mn concentrations over 100 ppm.

All of the Maritime lakes had residual zinc concentrations below 25 ppm. Carter, Loon, and one of the Triangle Lake cores had concentrations below 10

ppm. Except for Big Lake, residual Zn concentrations in the montane lakes were similar to those found in the Maritime lakes. Blue, two of the three Suttle Lake cores, Todd, the Newberry Caldera lakes, Morgan, and one of the two Walton Lake cores had concentrations below 10 ppm; Lava at 1.5 ppm was the lowest. All of the other lakes except for Big Lake had residual Zn concentrations between 11 and 22 ppm. The north station of Big Lake once again had the highest concentration, 54 ppm; the deep station averaged 29 ppm.

Residual copper did not vary greatly in these lakes. Concentrations in maritime lakes varied from 1.5 ppm in one core from Carter Lake to 13.9 ppm in one sample from Clear Lake. The means varied between 3.9 ppm in Carter to 8.0 ppm in Loon. Except for Big Lake, the Wizard Island shelf sample, and Lake of the Woods, none of the montane lakes had Cu concentrations greater than 10 ppm. Paulina had an average of 1.3 ppm, East an average of 1.5 ppm and Lava's mean concentration was 3.4 ppm. Big Lake, except the north station, Lake of the Woods and the Wizard Island shelf sample were between 15 and 17.5 ppm. The north station of Big Lake had a residual Cu value of 37.4 ppm.

Residual cobalt was also relatively stable in the lakes sampled. All of the coastal and Willamette Valley lakes averaged between 20.5 ppm Co (Carter) and 41.1 ppm (Loon) as did a few of the montane lakes. Most of the mountain lakes had residual concentrations below 20 ppm. The three lowest were Lava (0.3 ppm), Todd (6.1 ppm) and Paulina (7.4 ppm). Even the north station of Big Lake, the second highest residual Co value in the montane lake cores, was less than 40.3 ppm. The other high values were from Squaw (40.7 ppm) and the Wizard Island shelf (37.1 ppm).

The concentrations of sedimentary residual nickel in these lakes typically ranged between 7.5 and 31.0 ppm; the mean of all residual Ni concentrations was 19.2 ppm. The outliers were Lava (0.2 ppm), East (6.3 ppm), Paulina (5.1 ppm), Lake of the Woods (35.0 ppm), Squaw (41.7 ppm) and the north station of Big Lake (47.9 ppm).

Almost all of the mean residual vanadium concentrations from the coastal and Willamette Valley lakes were between 30 and 75 ppm (Mercer averaged 71 ppm and the northeast bay station in Woahink was only 28 ppm). Carter at 14 ppm was the only lake clearly outside of this range. Most of the

mountain lakes had lower residual V concentrations. The lowest concentrations were in Todd (0 ppm!), East (11), Paulina (10), and Lava (14). Big and Squaw Lakes were considerably higher at 113 and 106 ppm respectively than either the western Oregon lakes or the mountain lakes except the north station of Big Lake at 165 ppm. Crater, Suttle and both Blue Mountain lakes had residual V concentrations which were similar to that of the western Oregon lakes.

Two different residual extraction methods were used on eight cores from four lakes, Carter, Clear, Big and Suttle. The method used on the sediments from all of the lakes was ashing the dried residue from the HCl digestion, then dissolving about 1 gm of ash in HF. This method was back calculated to correct for the weight loss upon ashing. The second method, wet digestion with a combination of perchloric acid and HF, produced lower concentrations; the mean value was 0.85 of the first even including the correction used in the first method. There was, however, great variability between different cores; mean core values ranged from 0.46 to 1.34. The highest was from Carter #2, which had a large amount of small pieces of wood present. The second highest core mean, 1.30, was from the north station of Big Lake. With the exceptions of Ni and V from Big Lake #2, none of the other residual ratios of wet/dry ash were over 1.06.

9. Water column molybdenum concentrations

The concentration of filterable molybdenum in the epilimnion of the 21 lakes in this study are presented in Appendix C. The mean concentration was $3.4 \pm 2.9 \text{ nmol} \cdot \text{l}^{-1}$. Molybdate-Mo concentrations were significantly higher than average in Paulina, Clear, Oswego, Squaw and Morgan Lakes and significantly lower than average in Eel, Woahink, and Big Lakes. The maximum value observed was $8.6 \text{ nmol Mo} \cdot \text{l}^{-1}$ in Paulina Lake and the minimum observed concentration was $0.1 \text{ nmol Mo} \cdot \text{l}^{-1}$ in Big Lake.

C. Sedimentation Rates

One lake, Todd, of the 21 studied for trace metal fractionation had a directly measurable sedimentation rate while the average rate for five more of the 21 was calculated based upon stratigraphic events. The five lakes with calculated sedimentation rates were Woahink in the Coastal ecoregion, Oswego in

the Willamette ecoregion, Blue in the Santiam Pass area of the Cascades ecoregion, South Twin in the Eastern Transition ecoregion, and Walton in the Blue Mountain ecoregion. Two more lakes, not studied for trace metals, also had calculable sedimentation rates, North Twin, next to South Twin, and Dorena Reservoir in the Willamette ecoregion, near Cottage Grove.

The Todd Lake sediments were unique among the 49 lakes sampled as they had annual varves. The mean thickness of these varves was 0.4 ± 0.1 mm. A pale, coarse powder, apparently volcanic in origin, occurred in a band between 7.5 and 7.7 cm. Using the mean thickness of the varves as a dating device, a raw date of between 1796 and 1801 was calculated for this eruption. After subtracting the 1.8 to 2.0 cm floc layer from the core length, an estimated eruption date of 1846 was obtained.

Woahink was cored three different times in two places, March 1985, July 1986, and September 1989 in the middle of the lake and in the northeast arm (Figure 3). On all three occasions the same horizontal and vertical pattern was found. Vanadium increased over the background beginning at 10 cm depth in the station at the middle of the lake (Figure 9). However, when the increased V concentration is standardized to the background total Al concentration, the increase does not begin until the 4 cm depth (Figure 15). This phenomenon, which did not occur in either Munsel or Eel Lakes, is probably due to increased rates of fine particulate deposition from petroleum combustion (Baron, et al. 1986, Charles and Norton 1986) beginning sometime between 1930 and 1950. Using 1945 as the most likely detection date, this means that a minimum of 40 mm were deposited in Woahink between 1945 and 1985, or $1.0 \text{ mm}\cdot\text{yr}^{-1}$.

Two long cores were collected from Lake Oswego for purposes other than this dissertation. These two cores sampled the entire length of sediment deposited in Lake Oswego since the construction of the dam. The total thickness of sediment formed between about 1912 and 1985 was 220 to 230 cm, though probably most of it originated since the canal from the Tualatin was cleared, widened, and deepened in 1948. The average sedimentation rate for the entire time period that Lake Oswego has existed was 30.1 to $31.5 \text{ mm}\cdot\text{yr}^{-1}$. If 75 to 90% of the sediments have been deposited since 1948, a logical conclusion is that both the canal "improvements" occurred and lawn fertilization rates increased after the Second World War and complaints about nuisance algae

Figure 15. Vertical profile of the V:Al ratio in Woahink Lake sediments.

also increased in frequency during this period, then the recent annual sedimentation rate is between 44.6 and 55.9 mm.

Both South and North Twin Lakes were first sampled in 1986 and South Twin was re-cored in 1989. The two lakes are separated by an 800 m wide ridge less than 100 m high and they possess identically appearing sediments. North Twin Lake has a distinctive volcanic ash and tefra layer centered at 75 cm. Signs of this layer occur as low as 78.5 cm and as high as 60 cm. A second, smaller layer of ash is present at 55 cm. Neither South Twin core #3 nor #4, the analyzed ones, had a length over 30 cm due to the shorter corer used in re-sampling this lake, so these layers are not present in the analyzed cores. However, the same layers were found in the first two cores taken from South Twin at slightly shallower depths than they occurred in North Twin (<5 cm higher). According to W. Scott of the Cascades Volcanic Observatory, Vancouver, WA (1987, 1990 personal communication), there were two major eruptive episodes of South Sister between 2300 and 2000 years BP, separated by a dormant period of roughly two centuries. The second eruption of South Sister apparently coincided with the last important Newberry Caldera eruption of about 2050 yrs BP (Johnson, et al. 1985). If the main ash layer at 75 cm in North Twin and a little over 70 cm in South Twin is assumed to be from the earlier eruption, and the weak signs represent the 2000 yrs BP eruptions of either South Sister or the Newberry Caldera (probably of South Sister as the prevailing wind at the time of the Newberry eruption was from the west - Priest 1986 personal communication), then the average rate of sedimentation for these two lakes was $0.3 \text{ mm}\cdot\text{yr}^{-1}$. This rate remained nearly constant between the two eruptive events and between the two lakes with South Twin having just a slightly lower rate.

A thin, gray ash layer was found in Blue Lake 46.5 cm below the sediment-water interface and two more were observed deeper in the first pair of cores from this lake; the deepest one was between 80 and 85 cm. The nearby Belknap Crater (15.6 km southwest) erupted >2900 yrs BP, 2883 yrs, 1775 yrs, 1495 yrs, and 1330 yrs BP (Wood and Kienle 1990) as well as several more earlier; however, Blue Lake formed only 3500 yrs ago. The top ash layer was probably from either the 1495 or 1330 yrs BP eruptions, yielding an average sedimentation rate of 0.35 or $0.31 \text{ mm}\cdot\text{yr}^{-1}$. If the lowest layer observed was

from either the first two events, then the sedimentation rate for the longer length was about 0.28 mm per year. These calculations indicate that Blue Lake has a roughly 0.3 mm·yr⁻¹ rate.

Walton Lake was constructed in the 1940's (Johnson, et al. 1985) and cored in 1989. There was between 6 and 7 cm of lake sediment on top of the original soil. Using 1946 as the estimated completion date, the average sedimentation rate was between 1.4 to 1.6 mm·yr⁻¹ for this small mesotrophic reservoir.

Dorena Reservoir was finished by the Corps of Engineers in 1949. It was cored in July 1985 near the deepest part, close to the dam face. The second core taken there had a length of 44 cm. The lowest 4-5 cm was the original soil beneath the lake sediments, thus in the 36 years since the dam was completed, 39-40 cm of sediments have been formed in this lowland mesotrophic lake. This produced an average sedimentation rate between 10.8 and 11.1 mm·yr⁻¹.

D. Sedimentary Diatom Composition

1. Common Species

Fifty-six of the 114 species of diatoms found in the sedimentary samples (Appendix B) were represented among the ten most common diatoms in the study lakes; however, only 13 species comprised over 60% of the occurrences (Table 6). The commonest species found in the sediments were *Asterionella formosa*, *Fragilaria construens*, *F. crotonensis*, *F. pinnata*, *Synedra radians*, *Achnanthes minutissima*, *Cocconeis placentula*, *Melosira ambigua*, *Cyclotella meneghiana*, *C. stelligera*, *Stephanodiscus hantzschii*, *S. minutulus*, and *S. transylvanicus* (Table 7). These 13 species demonstrated several broad, ecoregion-based patterns which the subsequent cluster analysis quantified.

Asterionella formosa demonstrated one pattern (Table 7). It had a relative abundance greater than 5% only in Crater, East, Paulina, and Squaw Lakes, i.e., the deep caldera and Siskiyou lakes. The three *Fragilaria* species, in contrast, typically had relative abundances over 20% only in the Cascades and Eastern Transition ecoregion lakes, excluding Big, Lake of the Woods, and the Newberry lakes, but including Walton. The only outlier to this pattern was the 36.5% relative abundance of *F. crotonensis* in Oswego.

Table 6. Ten more common diatoms found in the sediments of the study lakes

Lake: Carter%	Eel %	Woahink %	Mercer %	Triangle %	Loon %
1 ACMN 31.2	CCST 27.8	CCST 18.6	MLGR 30.6	CCST 21.1	ACMN 16.2
2 STHN 7.4	STMN 14.3	STHN 13.0	STHN 18.5	MLGR 11.2	SNRD 7.5
3 FRPN 7.2	MLIT 14.2	EUIN 10.4	STTS 12.6	STHN 10.9	FRCR 6.8
4 NVVR 7.1	STTS 6.4	COPC 9.8	CCST 10.7	STTS 10.3	STHN 6.1
5 COPC 5.6	SNUL 5.8	NVCR 7.4	FRCN 4.6	FRCR 8.9	ACLC 5.9
6 SNUL 5.5	CCMG 5.3	CCMG 3.4	MLIT 4.3	TBFN 5.7	COPC 5.8
7 ACST 4.9	FRCR 3.5	KSXX 3.0	MLAM 4.1	ACMN 3.9	ACLN 5.4
8 CCST 3.2	ACMN 3.1	TBFN 2.8	FRCR 2.4	SNUL 3.0	NVVR 5.2
9 NVCR 2.8	TBFN 2.7	EPTR 2.7	STAL 1.4	COPC 2.8	CMMN 4.8
10 MLIT 2.7	STHN 2.1	SULN 2.6	KYDB 1.3	SNRD 2.7	SNUL 4.7
AFPR 2.7	85.2	73.7	90.5	80.5	68.4
77.6					

Lake: Clear%	Oswego %	Big %	Blue %	Suttle %	L.Woods%
1 CCMG 22.0	FRCR 36.5	MLGR 34.9	MLAM 31.7	FRCN 23.6	MLAM 79.4
2 STHN 18.4	STNG 24.6	STHN 22.0	CCKR 18.7	STTS 21.1	STHN 4.8
3 FRCA 13.5	SNRM 8.8	PLMC 12.7	MLIT 16.3	FRCR 13.8	FRCN 3.0
4 SNRM 8.4	MLAM 7.8	SULN 10.6	FRCN 15.9	STNG 13.0	CCST 2.7
5 MLAM 7.6	FRCA 7.6	PLSD 6.2	ASFO 4.3	CCKR 4.8	TBFN 1.4
6 FRCR 6.8	ASFO 5.0	FSRH 2.2	FRPN 3.6	MLAM 4.4	SNRD 1.1
7 ASFO 4.5	STHN 2.8	NVVR 1.5	STMN 1.8	SNRM 2.3	EUPM 0.9
8 MLDS 3.8	CCMG 1.1	FRCR 1.4	MLDS 1.0	ASFO 2.1	CCMG 0.8
9 COPC 1.8	NZPL 0.8	ACMN 0.9	EPTR 0.8	STAL 2.1	ACMN 0.6
10 SNRD 1.8	ACMN 0.6	EUIN 0.6	ACMN 0.7	STMN 1.7	FRPN 0.6
88.6	95.6	93.0	94.8	88.9	95.3

Lake: Crater %	East %	Paulina %	Lava %	S. Twin %	Todd %
1 FRPN 21.0	STTS 51.4	STTS 54.7	FRPN 33.2	STHN 23.8	FRPN 36.1
2 EPMU 11.6	ASFO 11.4	ASFO 20.3	FRCN 31.3	FRCR 12.5	FRCN 32.4
3 FRCN 8.4	FRCN 6.4	FRCN 4.9	SNRD 9.6	TBFN 10.1	STHN 15.8
4 ASFO 8.0	STMN 6.0	STMN 3.6	STNG 7.3	FRCN 9.8	MLIT 3.0
5 STPR 7.4	COPC 3.8	STHN 3.0	STMN 6.9	FRPN 8.7	ACMN 2.0
6 NZGR 7.4	STHN 2.7	FRPN 2.9	STHN 2.1	MLAM 8.3	ASFO 1.4
7 COPC 5.1	EPTR 2.7	FRCR 1.5	FRBR 2.0	NVPP 7.4	CCST 1.1
8 EPTR 4.9	FRBR 2.5	COPC 1.2	NZAM 1.4	AFOV 3.1	HNAR 0.9
9 GFSB 3.1	FRPN 1.2	AFPR 0.9	FRVI 1.3	NDXX 2.0	GFSB 0.6
10 ACMN 2.7	CODS 1.2	FRBR 0.8	CMXX 1.0	CCMG 1.6	NVVR 0.5
79.6	89.3	93.8	96.1	87.3	93.8

Lake: Walton %	Morgan %	Squaw %
1 FRCN 11.4	MLGR 28.0	ASFO 31.1
2 FRPN 9.6	SNRD 20.2	FRCR 9.9
3 MLGR 6.3	STMN 14.5	STPR 9.8
4 COPC 5.4	STNG 10.4	SNRM 8.7
5 NVVR 4.8	CCMG 6.6	SNRD 5.6
6 NZPC 4.2	STHN 2.8	FRCA 5.6
7 NZAM 4.1	FRCN 2.1	MLAM 4.6
8 STHN 4.0	PLMC 1.6	ACMN 2.9
9 NZFR 4.0	SNUL 1.4	CCMG 2.9
10 FRCR 3.7	NZLN 1.1	STTS 2.8
57.5	88.7	83.9

Table 7. The 13 Most Abundant Diatoms Found.

Lake	ASFO	FRCN	FRCR	FRPN	SNRD	ACMN	COPC	MLAM	CCMG	CCST	STHN	STMN	STTS	Total
Carter	-	-	0.7	7.2	1.3	31.2	5.6	-	-	3.2	7.4	-	+	56.6
Eel	-	0.6	3.5	-	1.9	3.1	2.4	-	5.3	27.8	2.1	14.3	6.4	67.4
Woahink	0.6	-	-	-	2.1	0.8	9.8	0.3	3.4	18.6	13.0	0.6	+	49.2
Mercer	0.9	4.6	2.4	-	0.2	0.3	0.6	4.1	0.3	10.7	18.5	-	12.6	55.2
Loon	1.2	0.4	6.8	0.2	7.5	16.2	5.8	0.1	0.1	4.4	6.1	0.1	-	48.9
Triangle	1.7	-	8.9	-	2.7	3.9	2.8	-	-	21.1	10.9	1.0	10.3	63.3
Clear	4.5	0.2	6.8	-	1.8	0.7	1.8	7.6	22.0	1.5	18.4	0.7	-	66.0
Oswego	5.0	0.1	36.5	-	0.4	0.6	0.2	7.8	1.1	0.6	2.8	-	-	55.1
Big	+	0.2	1.4	0.1	0.5	0.9	1.9	-	0.1	-	22.0	-	-	27.1
Blue	4.3	15.9	0.2	3.6	0.1	0.7	-	31.7	-	-	-	1.8	-	58.3
Suttle	2.1	23.6	13.8	-	0.4	0.8	-	4.4	-	-	-	1.7	21.1	67.9
Lava	-	31.3	-	33.2	9.6	0.2	0.5	-	-	-	2.1	6.9	-	83.8
Todd	1.4	32.4	-	36.1	0.5	2.0	0.4	0.1	0.3	1.1	15.8	-	-	90.1
L. Woods	0.5	3.0	-	0.6	1.1	0.6	0.4	54.7	0.8	2.7	4.8	-	-	69.2
Crater	8.0	8.4	1.4	21.0	-	2.7	5.1	-	0.2	-	-	0.4	0.2	47.4
East	11.4	6.4	0.9	1.2	0.5	0.9	3.8	-	-	-	2.7	6.0	51.4	85.2
Paulina	20.3	4.9	1.5	2.9	0.2	0.5	1.2	-	-	-	3.0	3.6	54.7	92.8
S. Twin	-	9.8	12.5	8.7	+	0.6	0.6	8.3	1.6	-	23.8	-	0.2	66.1
Walton	-	11.4	3.7	9.6	3.6	3.2	5.4	-	0.1	-	4.0	-	0.3	41.3
Morgan	-	2.1	-	0.4	20.2	0.2	0.3	-	6.6	-	2.8	14.5	1.0	48.1
Squaw	31.1	0.3	9.9	+	5.6	2.9	1.2	4.6	2.9	0.1	1.3	-	2.8	62.7

Mean=62.0
SD= 16.5

Key: + means <0.1%; - means absent.

Barring *F. crotonensis*, ten of the remaining diatoms had very similar abundances between Oswego and Clear Lakes. However, both *Cyclotella meneghiniana* and *Stephanodiscus hantzschii* had much higher relative abundances in Clear Lake than in Oswego. The relative abundance of *C. meneghiniana* in Clear Lake was unusually high as nowhere else did it achieve a relative abundance over one-third of that found in Clear Lake.

Another pattern was demonstrated by *Cyclotella stelligera*. It had a relative abundance over 3% only in lakes of the Coastal ecoregion. It was less common in the Willamette ecoregion, and was absent from all montane lakes except Squaw, Lake of the Woods and Todd.

Significantly lower relative abundances of the 13 common diatoms were found in Big Lake compared to all other study lakes (over 2 standard deviations less - Table 7). Seven of the ten commonest species in the sediments of Big Lake are not widely distributed, and only the common species, *Stephanodiscus hantzschii*, possesses a high relative abundance. The seven species with more restricted requirements are *Melosira granulata*, *Pinnularia microstauron*, *Surirella linearis*, *P. sudetica*, *Frustulia rhomboides*, *Navicula viridula*, and *Eunotia incisa*. These seven species comprise over 70% of the frustules found in Big Lake sediments. This lack of similarity between the diatom flora of Big Lake and the other lakes suggests that it may possess a distinct assemblage.

2. Some Interesting Finds of Less Frequently Occurring Species

In addition to *Cyclotella stelligera*, several other, less common species characterized the lakes of the Coastal ecoregion by their presence or relative abundance. These included *Coscinodiscus* sp. which was found only in Carter, Eel, Woahink, Mercer, and Squaw (!), *Tabellaria fenestrata* in relative abundances over 1.0% in all 6 lakes of this ecoregion as well as in Lake of the Woods and South Twin (where it attained its maximum relative abundance of 10.1%), and *Synedra ulna*, which had a relative abundance $\geq 3.0\%$ in four of the six lakes while reaching a maximum of only 1.4% elsewhere. A second much rarer *Synedra*, *S. parasitica*, also helped define the Coastal ecoregion by its absence; it was found in 10 of the remaining 15 lakes.

Another species of *Synedra*, *S. rumpens*, also had a characteristic distribution pattern. Its relative abundance exceeded 8% in only three lakes, Clear, Os-

wego, and Squaw. No other lake had more than 3%. Another species of *Synedra* with a characteristic pattern was *S. mazamaensis*. This species was found in four lakes, Crater, where it was first described, Blue, Suttle, and Lake of the Woods. Other unusual species of Crater Lake include *Epithemia muelleri* (found in only two other lakes in much lower densities), *Nitzschia gracilis* (found in three other lakes in much lower densities), and *Stephanodiscus parvus* (also found in Squaw Lake in similar relative numbers).

The common species of East and Paulina Lakes were nearly identical both as to species and to rank order (Table 6). The first four species of both lakes were *Stephanodiscus transylvanicus*, *Asterionella formosa*, *Fragilaria construens*, and *S. minutulus*. The next five species found in East Lake, *Cocconeis placentula*, *S. hantzschii*, *Epithemia turgida*, *F. brevisstrata*, and *F. pinnata* were also among the next seven species found in Paulina Lake. The only exceptions to this pattern were *Cocconeis disculus*, the tenth commonest species in East Lake, and in Paulina Lake, *F. crotonensis*, the seventh most common species, and *Amphora perpusilla*, the ninth most common species.

Most of the frustules found in the sediments of Lake of the Woods belonged to *Melosira ambigua*, 79.4%; the only other lakes with a single species comprising over 50% of the sedimentary remains were East and Paulina. Lake of the Woods possessed an odd pattern of sedimentary diatoms (Table 6), similar to its unusual phytoplankton (Sweet 1994 personal communication).

In summary five montane lakes had distinctive diatom compositions due to one reason or another separate from the Coastal lake group and the majority of montane lakes. These five were Big, Crater, Lake of the Woods, Squaw and probably South Twin. Oswego may have been different from other lakes in the Willamette Valley, but this could not be determined without more replicates.

3. Descriptive Observations of Relative Sedimentary Abundances

Although the numbers of frustules per mg of lake sediment were not systematically recorded, there were several important observations made during the diatom counts which had later significance in the data analyses.

Sediments from both Blue and Suttle Lakes, along with several other lakes, were examined under a microscope before digestion. Diatom frustules

comprised an estimated 80 and 90 percent of the volume of Blue Lake sediments and only slightly less of the total volume for Suttle Lake. The opposite characteristic was apparent in sediments from South Twin Lake. Although normal volumes of sediment (about 0.05 to 0.10 cm³) were digested, there was almost nothing on the slides. Instead of 10 to 40 fields producing 300 to 1000 frustules, each count required multiple rows of fields. The estimated diatom density per cubic centimeter was less than a tenth the typical values.

Another lake with low sedimentary densities of diatom frustules was Loon Lake. However, unlike South Twin where there was next to nothing else either, Loon Lake had high concentrations of clastic materials. This made identification difficult and may have biased the counts. Although the sediments of Carter Lake were mainly quartz grains by volume, so similar problems to Loon's might have been expected to be present and possibly more severe; the density of diatom frustules was considerably higher in this lake. Consequently, identification of adequate numbers of frustules from Carter was not a problem.

E. Statistical Analyses of the Chemical Data

1. Major ion water chemistry

Two different statistical analyses, partial correlation matrices (CM) and principal component analysis (PCA), were performed on the water chemistry data. The analyses examined the relationships between the seven major conservative parameters (Na, K, Ca, Mg, Cl, SO₄, and alkalinity) as well as conductivity, total dissolved P (tdP) and filterable Mo (Mo_{aq}). Similar results were found in both analyses. Three components emerged from PCA; Factor number 1 was dominated by positive loadings from conductivity, all four cations, and alkalinity; the predominant influences in Factor number 2 were positive loadings of tdP and Mo_{aq} with a negative loading from sulfate concentrations; while Factor number 3 was solely a positive chloride loading.

The independence of chloride and sulfate was also observed in the general (or zero order partial), first, and second order CMs as was the negative relationship between sulfate and Mo_{aq} and the positive one between tdP and Mo_{aq} (all of these findings were statistically significant). When alkalinity was controlled for in the CMs, only the cationic pairs of Ca with Mg and Na with K

were significantly (<0.05) correlated, though all cations significantly correlated with each other when chloride or sulfate were controlled for (Appendix E.12).

From these results, two tentative conclusions were reached. First, the four cations can be regarded as two variables after conversion to $\text{meq}\cdot\text{l}^{-1}$, divalent and monovalent cations. These two parameters are most strongly related to alkalinity, conductivity, and to each other. (However, subsequent statistical analyses of the trace metals produced clearer results when the four cations were left as independent variables.) Second, the positive relationship between tdP and molybdate suggests that the latter anion is utilized by organisms in lakes just as phosphorus is, as originally hypothesized about this element.

2. Sedimentary trace metal relationships

When just total available sedimentary trace metals were correlated, the only significant relationships found were Fe to Mn and Cu with Zn. When the total available trace metals were adjusted for the conservative anions and tdP using partial CMs, several more significant correlations appeared. Cobalt correlated with Fe and Ni in all cases, and most of the time with V, as did Fe with Ni and V. Cobalt also significantly correlated with Mn about half of the time. These were not the only observed effects of major dissolved ions upon sedimentary trace metal concentrations though. High concentrations of divalent cations were frequently correlated with different sedimentary trace metal extractions (to be discussed later). The latter were probably strictly correlative, not causal, in nature however. Including the 14 extractions other than just the total available revealed a more complicated situation.

Exchangeable Co was significantly and positively correlated with 11 of the other 20 fractions. No correlations were observed with Cu or Fe other than the exchangeable fractions, nor with any Mn form or with total available Ni and Zn. By contrast, CuEx positively correlated only with CoEx , NiEx and CuTA . Exchangeable Fe was positively correlated with all forms of Co, other forms of Fe, MnEx , organic Ni and Zn, and with total available V. MnEx had nine positive correlations and two negative ones. The positive relationships were with CoOr , CoTA , FeEx , FeTA , other Mn forms, and organic Ni; the two negative correlations were with ZnEx and VOr . Exchangeable Ni was positively correlated with nine other trace metal fractions, all forms of Co, exchangeable Cu

and Zn, the other forms of Ni, and non-exchangeable V. VEx was positively correlated with seven fractions, all forms of Co, other forms of V, organic Ni, and exchangeable Zn. It was negatively correlated with ZnTA. Exchangeable Zn was positively correlated with exchangeable Co and Ni and with all forms of V, but was negatively correlated with all forms of both Fe and Mn, except exchangeable Fe.

There were a number of correlations between different trace metals in the organic fraction other than with metals in the exchangeable fraction. The first matrix below summarizes the within-fraction correlations, while the second describes the organic to total available trace metal correlations.

	Co	Cu	Fe	Mn	Ni	V
Zn	+	+	+	0	+	0
V	0	0	0	0	+	
Ni	+	0	0	+		
Mn	0	0	0			
Fe	+	0				
Cu	+					

	Organic:	Co	Cu	Fe	Mn	Ni	V	Zn
	Co	+	0	0	+	+	0	0
	Cu	0	+	0	0	0	-	0
Total Avail.	Fe	+	0	+	+	+	-	0
	Mn	0	0	0	+	+	0	0
	Ni	0	0	0	+	+	0	0
	V	+	0	+	0	+	+	+
	Zn	0	+	-	0	0	-	+

Sedimentary nickel and summer epilimnetic filterable Ni were correlated from the nine study lakes which were also sampled by Collier. Organic Ni was the sedimentary fraction most strongly correlated with Ni_{aq} in these lakes (the correlation coefficient = 0.5865, with a probability of 0.048). The only other significant correlation between any forms of Ni was the previously mentioned one between the organic and total available fractions in the sediments.

Partial correlation matrices were also calculated for trace metal ratios within the exchangeable and organic fractions. Most of the significant relationships found were auto-correlations. The non-auto-correlations are listed in Appendix E; no patterns were found.

3. Distribution of trace metals by lake category

The distributions of the seven sedimentary trace metals were analyzed using the ten lake categories based upon lake chemistry and trophic status as treatment variables in one-way ANOVAs and with Scheffe's procedure for pairing group means. The results of these tests are presented in Appendix E., Tables 1 to 4; they are summarized here.

Exchangeable cobalt had an F ratio with a probability of randomness $P()$ of 0.0043, however, none of the groups were significantly (5%) different from each other using Scheffe's procedure. At the 10% level Group 1 (three high conductivity, oligotrophic lakes - Carter, Eel, and Woahink) were significantly different from Group 5 (one high conductivity, oligotrophic lake - Mercer). Group means were $4.35 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for Group 1 and $13.2 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for Group 5.

Although the ANOVA results for exchangeable Cu possessed a $P()$ of <0.0001 , only Group 10, the one soft water, high alkalinity, high tdp oligotrophic lake, Crater, had a significantly higher concentration than did all of the other lakes at the 5% level of Scheffe's procedure ($11.7 \mu\text{g}\cdot\text{g dry wt}^{-1}$ vs. means of between 0.79 and $3.08 \mu\text{g}\cdot\text{g dry wt}^{-1}$). The size of the F ratio combined with the fact that one of the groups is only a single lake (which generally meant a weaker correlation) indicated that this is a very statistically robust finding. South Twin, with a similar water chemistry to Crater Lake, had the second highest mean concentration, and the two other high P, oligotrophic lakes (Group 9, Blue and Lava) had the third highest value.

Sedimentary FeEx also had an F ratio with a $P()$ of <0.0001 . Group 5, Mercer, was significantly higher at the 5% level than five of the other groups, and significantly higher at the 10% level for two more. The groups at the 5% significance level were #4, two hard water, high alkalinity, oligotrophic lakes, East and Squaw ($89.2 \mu\text{g}\cdot\text{g dry wt}^{-1}$), #9, the two soft water, low alkalinity, high P, oligotrophic lakes, Blue and Lava (114), #10, Crater (146), #6, two soft water, low alkalinity, eutrophic lakes, Suttle and Morgan (149), and #8, three hard

water, high alkalinity, eutrophic lakes, Clear, Oswego, and Paulina (830). The additional groups at the 10% level were #7, a soft water, high alkalinity, eutrophic lake, Walton ($185 \mu\text{g}\cdot\text{g dry wt}^{-1}$), and #3, the soft water, high alkalinity, oligotrophic South Twin Lake (192). The mean exchangeable Fe concentration for Mercer Lake sediments was $4760 \mu\text{g}\cdot\text{g dry wt}^{-1}$.

A second group, #2, five soft water, low alkalinity, oligotrophic lakes, Loon, Triangle, Big, Lake of the Woods, and Todd, also had a significantly (5%) higher mean FeEx concentration ($3370 \mu\text{g}\cdot\text{g dry wt}^{-1}$) than those of Groups 4, 9, 6, and 8, i.e. all other lakes which are soft water and have a low alkalinity as well as all hard water, high alkalinity lakes. However Group 2's exchangeable iron concentrations were not significantly different from either those of the four high conductivity lakes nor of the three soft water, high alkalinity lakes.

Exchangeable Mn also had an ANOVA P() of <0.0001 . There were three significantly different group means at the 5% confidence level using Scheffe's procedure and two more at the 10% level. The differences were Group 9 ($7.58 \mu\text{g}\cdot\text{g dry wt}^{-1}$) vs. Mercer Lake (358) and Group #8 (321), and Group 8 vs. Group 6 (79.6); the additional differences at 10% were Group 9 vs. Crater Lake (295), and Group 8 vs. Group 2 (143).

Exchangeable nickel had an F ratio with a P() of 0.0058, but none of the groups were significantly different using Scheffe's procedure at the 10% level.

The ANOVA results for exchangeable V possessed a P() = 0.0020. There were two differences observed at the 10% level between Group 9 and Groups 4 and 1. The exchangeable V concentrations were $37.1 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for Group 9, 7.8 for Group 4 and 11.5 for Group 1.

Sedimentary exchangeable zinc had an F ratio with a P() of 0.0005. Two group differences were seen at the 5% level, between Group 9 and Groups 1 and 8. Group 4 was also different from Group 9 at the 10% level. The four group mean concentrations of exchangeable zinc were $11.7 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for #9, 1.55 for #4, 1.85 for #1, and 2.10 for #8.

As can be seen from these results, Scheffe's procedure is much more restrictive in its requirements than is a one-way ANOVA, as ANOVA results with P()s of 0.0020 or less are required before any group differences at the 10% level appear using Scheffe's procedure. This restriction was kept to compensate for low numbers of lakes in the different groups.

The only significant group differences observed for organic Co were between Mercer and Groups 9 and 2. The means were $9.80 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for Mercer Lake, 1.84 for #9 and 3.26 for the soft water, low alkalinity, oligotrophic lakes.

All of the soft water, low alkalinity lakes as well as the oligotrophic high conductivity lakes had significantly (10%) lower organic Cu than Group 8. The group means were $24.9 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for Group 8, 2.67 for #9, 3.81 for #6, 5.32 for #1, and 7.05 for Group 2.

Organic Fe concentrations were significantly higher for East and Squaw Lakes than for all other lakes, while the high P-oligotrophic lakes had the lowest concentrations (exchangeable Fe concentrations for these groups were also quite low, the second and third lowest of the ten classes analyzed). The mean organic Fe concentration for East and Squaw Lakes was $1860 \mu\text{g}\cdot\text{g dry wt}^{-1}$. The next highest was Group 2 at $544 \mu\text{g}\cdot\text{g dry wt}^{-1}$. The FeOr concentrations for the high P-oligotrophic lakes were 15.7 for Group 9 and $16.2 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for Crater Lake. The only differences between the contrasts were that the four groups with only one lake (Mercer, South Twin, Walton, and Crater) were not significant at the 5% level, but were at the 10% level.

Organic Mn concentrations were significantly (5%) higher in Group 8 than four others, #9, #6, #1, and #2, and than South Twin at the 10% level. Group means were $724 \mu\text{g}\cdot\text{g dry wt}^{-1}$ for Paulina and the Willamette Valley lakes vs. 4.08 for Blue and Lava, 14.3 for Suttle and Morgan, 47.6 for the three oligotrophic high conductivity lakes, 62.7 for the soft water, low alkalinity, oligotrophic lakes, and 22.3 for South Twin. The second highest average concentration was found in Group 4, the two hard water, high alkalinity, oligotrophic lakes.

The analysis of variance results for organic Ni were same as those for exchangeable Ni, i.e., while there were apparently significant between-group differences, none were identifiable using Scheffe's procedure.

The highest concentration of organic V was found in South Twin, $137 \mu\text{g}\cdot\text{g dry wt}^{-1}$. This value was significantly (5%) higher than all other groups except #9, Blue and Lava Lakes, which had a mean concentration of 77.6 ppm. Group 9 was higher than four groups, Crater Lake ($4.78 \mu\text{g}\cdot\text{g dry wt}^{-1}$), #1 (12.0), #8 (12.5), and #4 (17.9). The group order for this extraction is rather interesting as while the hard water, high alkalinity groups are the 7th and 8th highest groups,

the two soft water, low alkalinity groups were the 3rd (#6 at 42.6 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) and 4th highest (#2 at 42.3). The high conductivity lakes were on either side of the hard water, high alkalinity lakes.

The only significant (10%) difference observed for organic Zn was between Mercer Lake (14.7 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) and Blue and Lava Lakes (0.53 $\mu\text{g}\cdot\text{g dry wt}^{-1}$).

The only significant (10%) contrast observed for total available Co concentrations was between Group 6 (39.3 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) and Group 9 (14.3).

Total available Cu had three significant (5%) differences, all between #8 (116 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) and other groups. The significantly lower groups, #1, 9 and 2, had mean concentrations of 17.5, 18.2, and 38.9 $\mu\text{g}\cdot\text{g dry wt}^{-1}$, respectively. The mean for Group 6 (29.6) was also significantly lower than Group 8 at the 10% level. The single lake groups of South Twin (21.1) and Mercer (33.0) were probably also significantly different, though not at the 10% level.

Total available Fe had seven significant (5%) contrasts; Mercer Lake (62,500 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) vs. Blue and Lava (1600), and both Groups 2 (51,400) and 8 (59,300) vs. Groups 9, South Twin (4680) and 6 (15,600). At the 10% level the contrast between Mercer and South Twin also became significant.

Five groups had significantly (5%) lower concentrations of MnTA than Paulina and the Willamette Valley lakes (2850 $\mu\text{g}\cdot\text{g dry wt}^{-1}$). Walton joined the previous groups at the 10% level; however the group composed of East and Squaw Lakes (943 $\mu\text{g}\cdot\text{g dry wt}^{-1}$), as well as Crater Lake (664), had high enough mean concentrations not to differ from Group 8.

Total available Ni had a similar pattern to organic Fe. East and Squaw Lakes were significantly (5%) higher than the other lakes (155 $\mu\text{g}\cdot\text{g dry wt}^{-1}$), while Group 8 had the second highest concentration at 65.8 $\mu\text{g}\cdot\text{g dry wt}^{-1}$.

South Twin Lake had significantly (5%) higher concentrations of VTA than did Group 1, and Group 2 was higher than both Groups 1 and 4. Mean concentrations were 258 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ for South Twin, 228 for the five soft water, low alkalinity, oligotrophic lakes, 83.4 for the three oligotrophic high conductivity lakes, and 108 for East and Squaw Lakes.

Total available Zn showed five significant (5%) between-group contrasts using Scheffe's procedure. Blue and Lava Lakes had a significantly lower mean concentration (17.9 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) than did Group 2 (109), Mercer Lake (113),

and Group 8 (120), while Group 1, at $51.1 \mu\text{g}\cdot\text{g dry wt}^{-1}$, was significantly lower than both Groups 2 and 8.

In summary, 31 group differences for seven exchangeable metals were identified from ten lake classes. Thirty-two contrasts were identified from metals extracted in the organic fraction, and 36 were found in the total available trace metals. It is noteworthy that *none* of the significant group differences were on the basis of trophic status, except for the limited condition of high phosphorus combined with oligotrophy. On the other hand, a number of the observed differences were on the basis of conservative water chemistry. Three different metal extractions (exchangeable and organic Fe as well as total available Ni) had significantly higher sedimentary concentrations in the five hard water lakes, particularly East and Squaw, than were found in the other lakes analyzed in this research, especially the three non-P-limited lakes. Organic Mn also tended to be higher in the hard water lakes.

A second series of contrasts was run between the ten lake classes which analyzed for their possible effects upon sedimentary trace metal ratios using the 42 calculated from the exchangeable and organic extractions. The ANOVA results are summarized in Appendix E, Tables 3 and 4.

Only two of the 97 significant differences from the exchangeable trace metal were between groups of lakes with the same conservative water chemistry and different trophic status, and there were only three trophic differences of 61 significant organic trace metal ratios observed in lakes possessing the same conservative water chemistry. These differences were exchangeable Co:Fe for Groups 2 and 6 and V:Co for Groups 3 and 7, and organic Co:Fe for Groups 2 and 6, Cu:Fe for Groups 4 and 8, and V:Co for South Twin vs. Walton (Groups 3 & 7). The low percentage of significant trace metal ratio contrasts found based upon trophic state supported the previous finding based upon absolute concentrations.

Because the lack of importance of trophic status to sedimentary trace metal concentrations was rather difficult to accept without further verification, a series of two-way ANOVAs were performed on the 21 metal

extractions. The covariates used to estimate trophic status were tdP and summer epilimnetic chlorophyll *a* concentrations (the results are in Appendix E.2). While either tdP or chlorophyll *a* concentrations or both possessed significant *F* values in 17 of the 21 extractions, only in eight of these were the significance levels equal to or better than the original significance levels for the lake classes alone. These eight were CoOr (significance of chl *a* = lake class), CoTA (chl *a* < lake class), MnOr (chl *a* < lake class), MnTA (chl *a* < lake class), NiOr (both chl *a* and tdP < lake class), VEx (tdP < lake class), VOr (tdP = lake class), and ZnEx (tdP < lake class). Thus, only these eight trace metal extractions had a stronger relationship to primary productivity in the 21 lakes studied than the extractions did towards conservative water chemistry as defined by the 10 lake classes.

These findings reveal two things. First, they support the conclusion that trophic status is not very important for sedimentary trace metals as 13 of the 21 extractions demonstrated none or less significant level of correlation to trophic status parameters. Second, it is noteworthy that half of the eight extractions with the higher levels of significance are from the organic fraction. This suggests that the hot peroxide treatment is mainly extracting organic material, and furthermore, that this material is probably the product of primary productivity from within these lakes.

As a consequence of these findings, a third series of lake chemistry contrasts was performed using a redefined set of lakes which lacked trophic status as a distinguishing characteristic (Results are summarized in Appendix E.5.). Five groups of lakes were identified, high conductivity lakes from the Oregon Coastal ecoregion (Woahink, Eel, Carter, and Mercer), soft water, low alkalinity lakes from the Coast Range, the Cascades, and the eastern Blue Mountains (Loon, Triangle, Big, Suttle, Lake of the Woods, Todd, and Morgan), soft water, high alkalinity lakes (South Twin and Walton), hard water, high alkalinity lakes from the Willamette Valley, the Siskiyou and the Newberry Caldera in the Eastern Transition (Clear, Oswego, Squaw, East, and Paulina), and non-phosphorus limited lakes (Crater, Blue and Lava).

There was only one contrast found with the redefined lake data set for cobalt, total available for the hard water lakes was significantly (10%) higher than it was for the non-P-limited lakes (35.1 vs. 19.7 $\mu\text{g}\cdot\text{g dry wt}^{-1}$).

The non-phosphorus limited lakes had a mean concentration of exchangeable Cu (5.41 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) which was significantly (5%) higher than the mean concentrations (1.09 to 1.99 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) for the other four groups of lakes. Organic Cu in the hard water lakes was significantly (10%) higher than in the soft water, low alkalinity lakes (16.7 vs. 6.13 $\mu\text{g}\cdot\text{g dry wt}^{-1}$). The three other groups had mean concentrations similar to the soft water, low alkalinity lakes (between 6.60 and 7.30 $\mu\text{g}\cdot\text{g dry wt}^{-1}$). The mean concentration of total available Cu for the hard water lakes (94.5 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) was significantly higher than three other groups, the high conductivity coastal (21.4 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) and soft water, low alkalinity (36.4 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) lakes at the 5% level and the two soft water, high alkalinity lakes (mean = 34.4 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) at the 10% level. The three non-P-limited lakes had a mean concentration intermediate to the contrasting groups (45.2 $\mu\text{g}\cdot\text{g dry wt}^{-1}$).

There were six significant (5%) contrasts of ten possible for exchangeable Fe. Both the coastal and soft water, low alkalinity lakes had higher mean concentrations (3120 and 2450 $\mu\text{g}\cdot\text{g dry wt}^{-1}$, respectively) than occurred in the other three groups (125 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ for the non-phosphorus limited lakes, 188 for the soft water, high alkalinity lakes, and 534 for the hard water lakes). The two low alkalinity groups were not significantly different. Organic Fe lacked significant contrasts, while total available iron had five. The mean concentration of FeTA found in the non-P-limited lakes (9830 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) was significantly lower than three of the other four groups, only the group mean concentration for the soft water, high alkalinity lakes (13,300) failed to be significantly higher. In addition, both the hard water lakes and the soft water, low alkalinity lakes were significantly higher than the soft water, high alkalinity lakes though the latter contrast had a reduced significance (10%).

Exchangeable Mn from the hard water lakes (264 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) was significantly (5%) higher than either the non-phosphorus limited lakes (103) or the soft water, low alkalinity lakes (125). Although a significant contrast was not found between the hard water and soft water, high alkalinity lakes, the mean concentration for the latter (110) indicated that the lack of significance was

due to sample size, not concentration. The hard water lakes also had significantly (5%) higher concentrations of both organic and total available Mn (579 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ vs. 31.4 to 58.7 and 2080 vs. 201 to 403, respectively).

No significant contrasts between redefined lake classes were found for either exchangeable or organic Ni. Total available Ni had the same pattern as Mn, the five hard water lakes were significantly (5%) higher than the other four groups (mean concentrations = 102 vs. 18.7 to 45.9 $\mu\text{g}\cdot\text{g dry wt}^{-1}$).

One significant (10%) contrast was found for exchangeable V, the mean concentration for hard water lakes (13.2 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) was lower than that of the non-phosphorus limited lakes (29.3). The high conductivity coastal lakes and the hard water lakes had significantly (5%) lower mean concentrations of organic V (14.2 and 14.6 $\mu\text{g}\cdot\text{g dry wt}^{-1}$, respectively) than occurred in the non-P-limited (53.3) and soft water, high alkalinity (80.7) lakes. The intermediate (42.4) soft water, low alkalinity lakes differed (at the 10% level) from all of the other lakes except the non-P-limited ones, two of which were also soft water, low alkalinity in terms of conservative water ion chemistry. The number of contrasts found for organic V was the largest of any observed, seven of ten possible. For total available V, the two soft water groups had significantly higher concentrations than did the high conductivity and hard water lakes ($\text{VTA}_{\text{SHA}} = 222.71$, $\text{VTA}_{\text{SLA}} = 205.23$, $\text{VTA}_{\text{HC}} = 98.87$, and $\text{VTA}_{\text{HHA}} = 134.15$ $\mu\text{g}\cdot\text{g dry wt}^{-1}$). The significance level for the soft water, high alkalinity - hard water contrast was only 10%, the rest were at the 5% level.

For yet again another metal, the mean concentration for the hard water lakes was significantly different than other lakes. Exchangeable Zn was significantly low than in the non-P-limited (5%) and soft water, low alkalinity (10%) lakes. The mean concentration for the hard water lakes was 1.88 $\mu\text{g}\cdot\text{g dry wt}^{-1}$; for the other two groups, they were 8.35 and 6.31, respectively. Organic Zn had a slightly different pair of contrasts, the high conductivity (mean concentration = 9.17 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) and hard water (7.09) lakes were significantly (at the 5 and 10 % levels, respectively), higher than the non-P-limited lakes (0.80). Three significant contrasts were found for total available Zn. Non-P-limited lakes had a lower mean concentration (30.9 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) than either the soft water, low alkalinity lakes (93.6) or the hard water lakes (104). The hard water

ZnTA concentration was also higher (10% level) than for the soft water, high alkalinity lakes (54.4).

Fifteen contrasts were observed for the exchangeable trace metals vs. the redefined lake classifications, 14 from the organic trace metals, and 24 from the total available trace metals. These results produced mean contrast per class values of 3.00, 2.80, and 4.80, respectively, with a grand mean of 3.53. A total of 53 significant contrasts were found, 35 of which involved the hard water lakes. If the hard water lakes are excluded from the analysis, the mean contrast per class drops to only 1.50. Furthermore, while the test sensitivity was reduced when the classes were combined, there was still between one and four more significant contrasts (specifically in the organic Fe results) where the hard water lakes differed from the others.

4. Distribution of trace metals by ecoregion

For the purpose of these analyses the Coastal Ecoregion was subdivided into the Coast proper and the Coast Range as the two sets of lakes had both very different water chemistries and very different origins. The former were unique among the study lakes while the latter were similar in their water chemistry, but not their origins, to those lakes found in the Cascades. The two Coast Range lakes were treated as a separate category for the purpose of determining the relationship(s) between the sedimentary trace metal concentrations of Coast Range lakes vs. the Coast lakes proper and the lakes of the Cascades.

Sedimentary cobalt did not have any strong relationships (See Appendix E.6). None of the ecoregions had distinctive exchangeable or total available Co contrasts at the 10% level using Scheffe's procedure. There were two significant (5%) contrasts for organic Co. The Coast Range lakes had significantly lower concentrations than did either the Coast lakes proper or the Eastern Transition lakes. Interestingly, organic Co for Squaw Lake was nearly equal to the mean concentration for Loon and Triangle Lakes (1.52 ppm vs. 1.24 ppm) while all of the other lakes, except those from the Coast proper and Eastern Transition ecoregions, had CoOr concentrations between 3.3 and 3.85 ppm.

Of the remaining 18 trace metal extractions, all possessed significant ANOVA results, and the significance level for 13 of the 18 was less than

0.01%. Of the remaining five, only exchangeable Cu and organic Fe had significance levels above one percent (1.8 and 1.7%, respectively). At least one ecoregion contrast was found at the 10% level using the Scheffe procedure for all 18 extractions; only exchangeable Cu and organic Zn lacked them at the 5% level. Specific statistical values are given in Appendix E.6; the description presented in the rest of this section will focus solely on results from Scheffe's procedure.

The seven Cascade lakes had significantly (10%) more CuEx than did the four Coastal lakes (3.61 ppm vs. 1.09). Lower concentrations were also present in the Blue Mountain and Coast Range lakes (0.87 and 0.94 ppm, respectively), but the number of lakes in these groups was too small to be significant. The amount of organic Cu in the Willamette lakes was significantly (5%) higher than in all other lakes, but this was due solely to the very high concentrations found in Oswego. The second highest ecoregion mean was found in the sediments of the seven Cascade lakes ($8.20 \mu\text{g}\cdot\text{g dry wt}^{-1}$). Several lakes contributed to the high average, particularly Big Lake and the Wizard Island shelf station of Crater. The total available Cu concentration was significantly higher in the Willamette Valley lakes (again due solely to Oswego) and in Squaw Lake than in the other 18 lakes (or more accurately, Oswego, Squaw and the Wizard Island Shelf core from Crater Lake had CuTA values over $100 \mu\text{g}\cdot\text{g dry wt}^{-1}$ while all other cores had values of less than $50 \mu\text{g}\cdot\text{g dry wt}^{-1}$). Total available Cu in Squaw Lake was significantly (5%) higher than lakes from the Eastern Transition and Coastal ecoregions, and at the 10% level for lakes from the Coast Range and Cascades; the amount of CuTA in the Blue Mountain lakes was not significantly (10%) different from Squaw Lake. The mean total available Cu concentration for the two Coast Range lakes was intermediate between the concentrations of this extraction from the Coastal and Cascade lakes (33.4 vs. 21.4 and $40.5 \mu\text{g}\cdot\text{g dry wt}^{-1}$, respectively). Average organic Cu concentrations for these three ecoregions had a different pattern however as the mean for the Coast Range lakes was lower than both the Coastal and Cascades lakes.

Both the Coastal and Coast Range lakes had significantly more exchangeable Fe than did the other lakes. Only the Willamette Valley lakes, though lower in concentration than the Cascade lakes, were not significantly different from the two Coastal ecoregions as was Squaw Lake from the Coastal lakes.

Small sample size probably caused this apparent lack of contrast since Squaw Lake had the second lowest concentration of FeEx found and the largest group of lakes, the Cascades, had the third highest mean concentration, yet was significantly lower than either of the Coastal ecoregions.

Due to high concentrations of iron in the peroxide extraction from East Lake, the Eastern Transition ecoregion had significantly more “organic” Fe than did the other lakes although the difference was significant (5% level) only for those lakes vs. those in the Blue Mountains. Both the Cascades and Coastal lakes had more “organic” Fe than did the Coast Range lakes. These differences however are probably due to iron sulfides being extracted along with the iron actually present in organic compounds as both East and Todd had “organic” Fe concentrations over $1000 \mu\text{g}\cdot\text{g dry wt}^{-1}$, while Paulina, Eel, and Mercer all had “organic” Fe concentrations greater than $100 \mu\text{g}\cdot\text{g dry wt}^{-1}$. Three of these five lakes have, or are suspected of having, sulfur springs, while the other two are located in an area with a subterranean flow of water with high iron concentrations present (Cooper Consultants 1985). Thus, not too much biological or biogeographical significance should be made of this finding.

Total available Fe was greater in Squaw Lake than in the Cascades at the 5% level of significance. There was also significantly (10%) more FeTA in the two Coast Range lakes than in the Cascades. The mean concentration for the Coastal lakes was intermediate between the Cascade and Coast Range lakes.

There was more exchangeable Mn in both the Eastern Transition and Coastal lakes than in the Cascade lakes (5% significance level). The Coast Range lakes had similar concentrations to the Coastal lakes proper. Except for Squaw Lake, the Eastern Transition lakes had significantly (5%) greater amounts of organic Mn than did all of the other lakes. There was very little difference in the concentration of organic Mn between the Cascade, Coastal, and Coast Range ecoregions. The MnTA results were identical to those of organic Mn except that the Cascade lakes had about half of the MnTA that the two coastal ecoregions did. The main cause behind all of these contrasts appeared to be very high Mn concentrations in all forms in the Newberry lakes, particularly Paulina.

There was more NiEx in Squaw Lake than in all of the lakes in western Oregon and the Blue Mountains. The concentrations found in both the Cascade

and Eastern Transition lakes were not significantly lower than was found in Squaw Lake. There was less in the Coast Range lakes than in either the Coastal or Cascades lakes, but the difference was not great (2.97 and 4.78 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ vs. 10.3 in the Cascade lakes). There was significantly (5%) more organic Ni found in the Eastern Transition lakes than in all other Oregon lakes studied. The Coastal and Cascade lakes were more similar to each other than either was towards the Coast Range lakes. Very high concentrations of total available Ni were found in Squaw Lake compared to all other lakes, 298 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ vs. only 31 to 56 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ for the other 20 lakes. The difference in NiTA concentrations between the Coastal, Cascade, and Coast Range lakes was small, only 31 and 41.8 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ for the Coastal and Coast Range mean concentrations while the Cascade lakes were intermediate.

Exchangeable V was significantly (5%) higher for the Cascade lakes when compared to Squaw and the Coast Range lakes and at a 10% level of significance between the Cascade and Willamette lakes. The next highest concentration of VEx, following Squaw, the Coast Range lakes, and the Willamette lakes, was found in the Coastal lakes (2.90, 3.88, 11.1, and 16.1, respectively, vs. 29.5 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ for the Cascade lakes). The Cascade and Eastern Transition lakes had significantly higher concentrations of organic V than the other lakes. Eight contrasts were significant at the 5% level; the contrasts between the Eastern Transition vs. Squaw and the Blue Mountain lakes were significant only at the 10% level. The mean organic V concentration of the Coast Range lakes was similar to that of the Coastal lakes. The only significant (5%) contrast for VTA was between the Cascade and Coastal lakes; the Coast Range lakes had the next lowest mean concentration. The mean values were 98.9, 129, and 214 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ for the Coastal, Coast Range, and Cascade lakes, respectively.

The mean concentration of exchangeable Zn was significantly (5%) higher for the Cascade lakes (9.32 $\mu\text{g}\cdot\text{g dry wt}^{-1}$) than for all other lakes except Squaw. The range of mean concentrations for all non-Cascade lakes including Squaw was between 1.32 $\mu\text{g}\cdot\text{g dry wt}^{-1}$ for the Coast Range lakes to 2.96 for the Coastal lakes. There was significantly (10%) more organic Zn in both the Willamette and Coastal lakes than was found in the Blue Mountain lakes. The

mean concentration of ZnOr in the Coast Range lakes ($2.10 \mu\text{g}\cdot\text{g dry wt}^{-1}$) was lower than found in the Cascade lakes (5.32) or in the Coastal lakes (9.17).

Total available Zn was present in significantly higher concentrations in the two Willamette Valley lakes (mean = $168 \mu\text{g}\cdot\text{g dry wt}^{-1}$) than in all lakes except Squaw ($138 \mu\text{g}\cdot\text{g dry wt}^{-1}$). ZnTA in Squaw was higher than in the Eastern Transition, Cascades, and Coastal lakes, while the Coast Range lakes had a significantly higher mean concentration ($108 \mu\text{g}\cdot\text{g dry wt}^{-1}$) than the Eastern Transition lakes ($28.6 \mu\text{g}\cdot\text{g dry wt}^{-1}$). The mean concentration for the Cascade lakes ($64.0 \mu\text{g}\cdot\text{g dry wt}^{-1}$) was more similar to that of the Coastal lakes (66.6) than either were to the mean for the Coastal Range lakes.

The following table shows the number of significant results for trace metal contrasts by group.

Extraction	Ecoregions (7)		Water chemistry classes (10)	
	total	ratio	total	ratio
Exchangeable	22	3.14	31	3.1
"Organic"	36	5.14	32	3.2
Total available	33	4.71	36	3.6
All extractions	91	13.0	99	9.9

The mean number of contrasts for all extractions was about 30 greater for ecoregions than for water chemistry classes. The number of groups was not significant in explaining the difference in the number of contrasts as the mean number of contrasts per group using the redefined lake classes (with only five rather than ten classes) was 10.6.

To order to verify the results from the previous section, an analysis of trace metal ratios by ecoregion was also performed (Appendix E., Tables 7 and 8). These results confirmed those given in the preceding paragraphs.

Two-way ANOVAs involving trophic status indicators, i.e., chlorophyll *a* and tdp concentrations, with ecoregions as the primary variable of interest even more strongly support the original conclusion that trophic status is not an important influence on trace metal distribution. The individual trace metal results (Appendix E.9.) were very similar to those found with the lake class

two-way ANOVAs. Phosphorus and/or chlorophyll *a* concentrations were statistically significant for 15 of the trace metal extractions; but the significance level of these co-factors was equal to, or lower than, the ecoregion effect for only seven of the extractions. The seven extractions were CoTA (chl *a* < ecoregion), MnOr, MnTA, and NiOr (chl *a* = ecoregion), and NiTA, VEx, and ZnEx (tdP = ecoregion). The only other noteworthy phenomena observed here were the much more significant results for the three Ni extractions and exchangeable Zn.

F. Cluster Analyses of Primary Producers

Cluster analysis, using the Ward minimum variance method with a distance metric of one gamma, was performed on both the summer phytoplankton and sedimentary diatom data.

For the summer phytoplankton data, the primary division was between the coastal and Coast Range lakes plus Lake of the Woods and Todd vs. other 13 lakes (Figure 16). The second major division within the “Coastal Plus” division was of the three oligotrophic Coastal lakes, Carter, Eel, and Woahink vs. the other five. The two Cascade lakes were the most similar within the “Coastal Plus” division. For the other 13 lakes, East, Paulina, South Twin, Walton, Morgan, Squaw, Lava, and Suttle were more alike to each than to the other five lakes. The Willamette Valley lakes split off next from the three oligotrophic alpine lakes, Big, Blue, and Crater, while the three Eastern Transition lakes were most distinctive subgroup of the main cluster.

With respect to the sedimentary diatom data, first, all of the samples from a given lake were more similar to each other than to any other sample. Second, the ecoregional similarity was even clearer and stronger than occurred in the summer phytoplankton data, probably due to the greater number of samples analyzed. The first division was between the six Coastal and Coast Range lakes vs. all others (Figure 17). Within the Coastal and Coast Range division, the most important separation was between these two groups. The second division split off Blue, Suttle, Squaw and the Willamette Valley lakes from the rest of the Cascade lakes and those in the Eastern Transition and Blue Mountains. The fourth division, in terms of distance, separated the two Santiam Pass lakes from the Willamette and Siskiyou lakes; the next one within this

Figure 16. Cluster analysis results based upon summer phytoplankton.

Dendrogram

Method is Ward Minimum Variance
Distance = 1-Gamma Coefficient

Figure 17. Cluster analysis results based upon sedimentary diatoms.

Dendrogram

group split off Squaw Lake from the other two. Returning to the main cluster, the third most important division split off the three deep caldera lakes, Crater, East and Paulina, from the others, while the fifth division separated Todd, Lake of the Woods, and South Twin from the Blue Mountain lakes, Lava, and Big.

G. Correlations between Primary Producers and Trace Metals

1. Effects on Summer Phytoplankton Numbers and Biomass

Initially the cell densities of 49 species, or taxonomically-based species groupings (i.e., multi-species taxa), of phytoplankton were analyzed against independent physical, water chemical, and trace metal parameters by stepwise multiple linear regression (MLR) as were biovolumes from 58 taxa (See Appendix B.1 for the list). Fifteen species by cell numbers were either not present in a sufficient number of the 21 lakes for analysis, or lacked any significant (at the 10% level) relationship with the independent parameters selected. Clearer results were demonstrated for the four remaining cyanophytes, two of the diatoms, and one green alga using biovolumes. Five other diatoms also had significant biovolume results but lacked valid results using cell numbers. The final set of analyzed summer phytoplankters consisted of 38 taxa; 20 diatoms, eight greens, four cyanophytes, four chrysophytes and two cryptomonads.

The principal independent variable from the four primary stepwise multiple linear regressions (all data vs. non-zero data only, and with or without trace metal ratios) for the final 38 summer taxa are presented in Appendix E.10. These results have not been corrected for outliers. Mean TSI, or the mean trophic status index, is derived from Carlson's (1977) indices, and is the average of Secchi Disc depth, chlorophyll *a* concentration, and total dissolved P concentration; the rest of the table labels are derivative abbreviations from the original parameters. Of the 20 species of diatoms examined, 11 had significant correlations as did seven of the eight green algae (possibly all eight). Three of the four chrysophyte flagellates and both cryptomonad flagellates also had significant correlations, while three of the four cyanophytes possessed distinctive patterns as well. A total of 26 significant findings were made; most of them were for both cell numbers and biovolumes when both were analyzed. The strongest findings were the relationships of *Anabaena flos-aquae*+

circinalis with organic Ni, *Staurostrum gracile* with VTA, *Sphaerocystis schröteri* with the organic Ni:V ratio, *Asterionella formosa* with Co, and *Cyclotella stelligera* with V. Equations relating individual summer taxa with their primary independent variable are presented in Table 8. Not too much should be made of these equations however, since first, the sample size is not particularly big (maximum N = 21) and second, with few exceptions, no transformations of the data were done. That is to say, for the most part these equations are indicative of a potential causal relationship worthy of further study, not predictive.

a. Diatoms

The summer abundance of *Asterionella formosa* is strongly correlated to the concentration of organic Co in lake sediments (Figure 18). When all of the summer data are included in the MLR model, the adjusted coefficient of determination (adj. R², i.e. the amount of variability explained by the parameter(s) in the regression model corrected for the number of variables included in the final equation) was 28.5%, and **no** other parameter of the initial 30 used (the 21 sedimentary trace metals, the seven conservative dissolved ions, tdP and mean TSI) entered the model. Further regressions were made which included exchangeable and organic trace metal ratios as well as Mo_{Aq}. The concentration of sedimentary organic Co remained the **sole** independent variable in the model. When just the non-zero density values of *Asterionella formosa* were included in the MLR model, a slightly different result occurred. Exchangeable Co became the sole independent variable explaining the variability of *A. formosa* cell numbers instead of organic Co. Again no other independent variables entered this regression, even when trace metal ratios and dissolved Mo were included. Exclusion of Mercer Lake increased the coefficient of determination from 52.4% to 67.2% (Figure 19), and added several secondary parameters to the model. The only ones with a higher F-value than the intercept were organic V and sulfate. Sedimentary organic Zn had about the same importance as the intercept, as was predicted based upon Reynolds and Hamilton-Taylor (1992).

When *Cyclotella stelligera* was first analyzed by MLR, the only statistically significant relationship found was between cell numbers and chloride concentration. The variability in [Cl] explained 49.7% of the variation in *C. stelligera* cell numbers. A plot of the data (Figure 20) revealed a striking pattern

Table 8. Primary regressions for the summer phytoplankton.

a. Diatoms	Equation	Adjusted R ² (in %)	N
ASFO (all)	= -17.4 + 9.62 * CoOr	28.5	21
ASFO (presence only)	= -47.9 + 12.7 * CoEx	52.4	11
CCST (all)	= -4.64 + 2.56 * Cl	49.7	21
CCST (from high Cl)	= -9.96 + 3.29 * VOr	66.4	8
CCST (from high Cl)	= -21.8 + 4.66 * ExVCu	88.0	8
CCRD (presence only)	= -3.00 + 1.46 * OrVCu	91.0	4
MLIT (presence only, no ratios)			
	= +209. - 27.0 * CoOr	62.6	6
MLIT (all)	= -16.4 + 2.48 * OrVCo	89.5	21
MLIT (presence only)	= -8.67 + 2.60 * OrVCo	98.5	6
ACMN (all)	= +5.57 - 0.12 * CoTA	29.5	21
ACMN (all with ratios)	= +0.46 + 1.00 * OrZnCo	37.2	21
ACMN (presence only)	= -0.27 + 3.68 * ExNiCo	60.0	12
NZFR (presence only)	= -1.05 + 0.11 * Alkalinity	55.6	8
SNRD (all)	= -2.51 + 0.08 * ZnTA	21.0	21
SNRD (presence only)	= -5.88 + 0.15 * ZnTA	44.6	10
SNRD (all with ratios)	= -1.09 + 2.78 * OrZnCo	27.7	21
SNRD (presence only, with ratios)			
	= -0.07 + 41.8 * OrZnFe	86.1	10
SNRD (presence only, with ratios)			
	= -2.20 + 5.83 * OrZnCo	80.6	10
[This is the second best parameter.]			
SNRM (presence only)	= +0.42 + 0.77 * ZnOr	23.6	10
SNRM (presence only, with ratios)			
	= +0.77 + 10.1 * OrZnV	51.8	10
SNUL-BV			
(all with ratios)	= +0.16 + 17.5 * ExCuMn	15.4	21
(presence only with ratios)			
	= +0.43 + 65.1 * ExCuMn	98.3	7
(presence only with ratios and without Suttle)			
	= +0.69 + 45.8 * ExCuMn	37.4	6

Table 8. Primary regressions for the summer phytoplankton continued.

a. Diatoms continued	Equation	Adjusted R ² (in %)	N
SNUL-BV continued			
(presence only)	= -1.52 + 1.77 * ZnEx	83.8	7
(presence only)	= -10.5 + 2.20 * CoEx	82.1	7
[This is the second best parameter.]			
	= +9.00 - 3.43 * CoEx + 0.35 CoEx ²	98.3	7
NZDS-BV (presence only)	= +.043 + .036 * ZnOr	93.7	5
NZAC-BV (presence only)			
	= +.007 + 59.5 * ExCuFe	60.3	7
Log ₁₀ NZAC-BV (presence only)			
	= -.271 -1.332*10 ⁻⁵ *FeTA	41.3	7
b. Chlorophytes	Equation	Adjusted R ² (in %)	N
SMGR (all with ratios)	= -13.2 + 7.70 * ExVCo	22.8	21
SLMN (all)	= -3.48 + 0.73 * CuOr	92.4	21
OCPU (all)	= -0.85 + 0.35 * CuOr	89.9	21
OCPU (presence only)	= +0.019 + 0.083 * CuTA	98.8	12
OCPU (all with ratios)	= -0.92 + 1.22 * OrCuCo	67.5	21
SFSR (presence only)	= +1.57 + 2.53*10 ⁻⁴ *FeTA	23.6	13
SFSR (all with ratios)	= +0.29 + 12.3 * OrNiV	23.1	21
SFSR (presence only, with ratios)			
	= +0.45 + 23.6 * OrNiV	75.5	13
AKFLSP (presence only, with ratios)			
	= -3.30 + 9.64 * ExVCo	32.1	18
OCLA (all)	= +0.14 + 5.78*10 ⁻⁴ *FeOr	68.0	20
OCLA (presence only)	= +0.78 + 4.00*10 ⁻⁴ *FeOr	85.7	6
SCDT-BV (presence only)			
	= +0.54 - 5.06*10 ⁻³ *ZnTA	95.3	4
CHXX (presence only)	= -1.09 + 0.84 * CoOr	70.7	7

Table 8. Primary regressions for the summer phytoplankton continued.

c. Cyanophytes	Equation	Adjusted R ² (in %)	N
ABFACR-BV (all)	= -20.4 + 7.02 * NiOr	51.0	21
(presence only)	= +1.17 + 7.60 * NiOr	60.0	8
ANMR-BV (all)	= -1.03 + 0.42 * Cl	31.2	21
ANMR-BV (presence only)	= +51.4 - 1.13 * NiTA	90.2	4
Log ₁₀ ANMR-BV (presence only)			
	= 3.637 - .531 * NiEx	80.1	4
ANXX-BV (presence only)	= +.275 - 1.92*10 ⁻³ *VTA	69.9	5
Log ₁₀ ANXX-BV (presence only)			
	= +.513 - .017 * VTA	73.4	5
d. Chrysophytes	Equation	Adjusted R ² (in %)	N
MMXX(all)	= +0.016+ 1.853*10 ⁻⁴ *FeEx	44.3	21
MMXX (presence only)	= -1.14 + 0.07 * CoTA	77.4	6
CYRF (presence only)	= -0.32 + .033 * FeOr	86.9	4
CYRF (presence only)	= -0.70 + 6.39 * OrCuV	98.3	4
KFSP (presence only)	= -0.14 + 0.13 * Ca	91.9	6
e. Cryptophytes	Equation	Adjusted R ² (in %)	N
RDMNLA (all)	= -113. + 4.88 * MeanTSI	31.3	21
RDMNLA (all)	= +21.8 + 470. * OrCoFe	38.5	21
CXER (all)	= -13.5 + 0.74 * MeanTSI	23.3	21
CXER (presence only)	= -7.32 + 20.0 * CuEx	29.6	14

Figure 18. Mean summer cell densities of *Asterionella formosa* vs. organic Co (in ppm-dry wt⁻¹).

Figure 19. Non-zero summer densities of *A. formosa* vs. exchangeable Co (in ppm·dry wt⁻¹).

Figure 20. Summer cell densities of *Cyclotella stelligera* vs. water column concentrations of chloride (in mg·l⁻¹).

however; the diatom was absent in waters with less than 5 mg Cl·l⁻¹. When just lakes possessing a chloride concentration greater than 5 mg·l⁻¹ were examined, organic V became the primary independent parameter (Figure 21), followed by chloride and exchangeable Zn. Excluding all null values for *C. stelligera* produced the same result, but the coefficient of determination dropped from 66.4% to 62.4% for just organic V, and from 95.4% to 92.8% for all three independent parameters. Adding trace metal ratios to the model did not alter the conclusion that chloride was the predominant influence on the abundance of *C. stelligera*. However, a negative exchangeable Cu:V ratio replaced organic V as the primary independent variable when only non-zero densities of *C. stelligera* were considered. If cell densities of *C. stelligera* are included from all lakes with a chloride concentration above 5 mg·l⁻¹, the adjusted R² for ExCuV drops to 8.4% and organic V again becomes the primary independent variable, explaining 73.0% of the variation in *C. stelligera* densities. Inverting the exchangeable Cu:V ratio increases the coefficient of determination from 73.1% for ExCuV in the original MLR using trace metal ratios to 88.0% for ExVCu (Figure 22). It is important to note here the very small difference in the coefficients of determination between organic V and the ExCuV ratio in the original trace metal ratio MLR, only 0.1%. Furthermore, when the ExVCu ratio is the primary independent variable, the ExVFe ratio, organic V and total available V are also enter the final regression equation. However, if only the Maritime lakes with chloride concentrations above 5 mg·l⁻¹ are included in the model (i.e., if Crater Lake is dropped from Figure 22), the adjusted R² due to ExVCu alone is 96.0%, the highest found in this research, with an F-value probability of less than 0.0001. To summarize, no cells of *Cyclotella stelligera* were found in Oregon lakes where the chloride concentration was less than 5 mg·l⁻¹, but in those lakes where this condition was met, sedimentary vanadium, particularly in the organic and exchangeable extractions, strongly correlated with the abundance of *C. stelligera*, explaining between 62 and 96% of the variation depending upon the form(s) of vanadium included in the MLR model.

Cyclotella stelligera was not the only species in this genus to possess a clear relationship with organic V. After the outlying Paulina Lake was removed from the two all lake MLR models, organic vanadium was the primary independent variable for *C. radiosa* (adjusted R² = 31.1%). However, the strongest

Figure 21. Densities of *C. stelligera* vs. organic V (in ppm·dry wt⁻¹) from lakes with [Cl] > 5 mg·l⁻¹.

Figure 22. Same as Figure 21, only compared with the exchangeable V:Cu ratio.

Figure 23. Non-zero summer densities of *Cyclotella radios*a vs. the organic V:Cu ratio.

relationship for the four lakes where summer populations of this species occurred was a non-linear regression with OrVCu (adjusted $R^2 = 91.0\%$, Figure 23). So although the relationship between organic V and *C. radiosa* is much weaker than it was between VOr and *C. stelligera*, nonetheless, it apparently still exists.

Other robust diatom findings (Table 8) included the relationship of *Melosira italica* with organic cobalt, especially the OrVCo ratio (Figure 24), *Achnanthes minutissima* with total available cobalt and the OrZnCo and ExNiCo ratios (Figure 25), *Nitzschia frustulum* with alkalinity, and *Synedra radians* with the OrZnCo and OrZnFe ratios (Figure 26). Only the first MLR model, of all lakes without trace metal ratios, lacked a correlation between *M. italica* and organic Co; the only model that did not have a primary *A. minutissima*-Co relationship was the second one, the presence only without trace metal ratios. Although alkalinity was the primary independent variable related to *Nitzschia frustulum* in both presence models and the strongest variable in the first model, the latter suggested a physiological response curve instead of a simple, always positive, relationship because the study lake with the highest alkalinity lacked this diatom. Both *Synedra radians* and *S. rumpens* primarily correlated with organic Zn or with ratios involving it. These two species and *Nitzschia dissipata* (Figure 27) were the only diatoms to have summer populations primarily related to zinc in the organic extraction, though it was also of secondary importance for both *Asterionella formosa* and *Achnanthes minutissima*.

Without the Eel Lake outlier in the two no-ratio MLR models for *S. rumpens* summer cell densities, the strongest independent variable for this diatom was organic Zn. The significance levels were weak, 6.4% (all) and 8.8% (non-zero values only) for these two regressions, although the relationship was definitely a pattern and not based upon a single outlier. When trace metal ratios were added to the list of independent variables for predicting the abundance of *S. rumpens*, the organic Zn:V ratio was the most important relationship found for both regressions (Table 8).

The summer biovolumes of *Synedra ulna* from the complete data set correlated only with the ratio ExCuMn (Figure 28). However, the high coefficient of determination (98.3%) for the non-zero values is largely due to the presence of a single high measurement in Suttle Lake since the adjusted R^2 is only

Figure 24. Non-zero densities of *Melosira italica* vs. the organic V:Co ratio.

Figure 25. Non-zero summer densities of *Achnanthes minutissima* vs. the exchangeable Ni:Co ratio.

Figure 26. Non-zero summer densities of *Synedra radians* vs. the organic Zn:Fe and Zn:Co ratios.

Figure 27. Non-zero summer biovolumes of *Nitzschia dissipata* vs. organic Zn (in ppm·dry wt⁻¹).

$$\text{NZDSBV} = .043 + .036 * \text{ZNOR}; R^2 = .952$$

Figure 28. Non-zero summer biovolumes of *Synedra ulna* vs. the exchangeable Cu:Mn ratio and exchangeable Co (in ppm·dry wt⁻¹).

37.4% without this lake. The best predictive parameter for the non-zero values of this species, in the absence of the trace metal ratios and including Suttle Lake, was exchangeable Zn (Table 8); the second best was exchangeable Co (adjusted R^2 of 82.1%, Figure 28). The last parameter still explained a moderate amount of the variation in the absence of Suttle Lake (35.1%), and it explained even more as a second order polynomial regression with Suttle Lake included (98.3%).

The last significant correlations found among the summer diatoms were two non-linear ones between *Nitzschia acicularia* biovolumes and Fe (Table 8).

These were the only important relationships found between summer diatom populations and the independent parameters measured. Neither of the two species of *Fragilaria* analyzed provided any new insights. The clearest pattern for members of this genus, though rather weak, was between the mean TSI and the non-zero summer cell counts of *F. crotonensis*. This weakness is probably due to the low numbers of mesotrophic to eutrophic lakes included in the present research (seven) as this diatom is well documented as being characteristic of such lakes (Hutchinson 1967, Johnson, et al. 1985, Reynolds 1984). Nor did the four taxa of *Stephanodiscus* studied, *Cyclotella krammeri*, *Navicula cryptocephala*, and the miscellaneous *Nitzschias* taxon display any clear patterns.

The only common diatoms in Oregon lakes (Johnson, et al. 1985), that were not analyzed from the summer phytoplankton counts were *Melosira granulata* and *Tabellaria* spp. The absence of *M. granulata* from this analysis was due to low numbers in the subset of lakes studied in this research, a purely chance happenstance. The latter genus tends to be commoner during the spring and fall in Maritime lakes (Macan 1970, Reynolds 1984), thus was not expected to be common in summer samples from Oregon.

b. Chlorophytes

Staurostrum gracile displayed a classical Gaussian distribution curve when plotted against total available V (Figure 29). The only null value between 150 and 225 ppm was the Oswego sample. Since *S. gracile* was common in Clear Lake and in many mesotrophic to eutrophic Midwestern lakes (Prescott 1957), possible effects of the copper additions to Lake Oswego were also

evaluated. Figure 30 suggests that *S. gracile* is copper intolerant. Its distribution is also related to the ExVCo ratio, however, the relationship appears to be considerably weaker as only 22.8% of the variability could be explained by this ratio (Table 8). The two highest nulls for the ExVCo ratio, both clear outliers in this relationship, are Blue and Lava Lakes, two of the three high phosphorus, oligotrophic lakes. Removing them from the data set resulted in a modest improvement as to the amount of variability explained, but in the absence of a specific mechanism could not be justified.

Conversely, both *Selenastrum minutum* and *Oocystis pusilla* appear to be quite tolerant of copper and reached their greatest summer abundance in Lake Oswego. Organic Cu was the primary independent variable correlated to the summer abundance of both species (Figures 31 and 32). Organic Cu was the primary variable for *S. minutum* in all MLR models except the complete data set with trace metal ratios where the OrCuFe ratio replaced the absolute organic Cu concentration. *O. pusilla* also correlated with the OrCuCo ratio (Figure 32) and CuTA (Figure 33) as well as the OrCuV and, less-so, the OrVCo ratios. Organic Cu, Co, and V all seemed to be important for *O. pusilla*, though Cu was clearly the primary metal influencing its distribution and abundance as nearly 90% (Table 8) of the variability of this species could be explained using just the sedimentary concentration of organic copper. Likewise, over 90% of the variability in numbers of *S. minutum* cells in the water column could be explained by the amount of “organic” copper in the sediments of the study lakes (Table 8).

No significant relationships were found for *Sphaerocystis schröteri* in the basic MLR model (using the entire data set with no trace metal ratios). This changed when either the eight nulls were removed from the model, or if trace metal ratios were added to either set (Table 8). The best fit was the OrNiV ratio in the non-zero model (Figure 34), it explained over three-quarters of the variability of this species (Table 8). This was primarily due to a strong non-linear negative relationship with organic V.

Minor discoveries among the green algae included the relationships of the taxon *Ankistrodesmus falculatus + spiralis* with the ExVCo ratio (Table 8), *Oocystis lacustris* with FeOr (Figure 35), the biovolume of *Scenedesmus denticulatus* with ZnTA (Figure 36), and possibly *Chlamydomonas* spp. with organic

Co (Figure 37) after an outlier from Clear Lake was removed. However, because the Clear Lake sample possesses the highest density found for *Chlamydomonas* spp. by nearly three orders of magnitude, exclusion of it is highly suspect so the correlation should be regarded as questionable, *unless* the high density is due to an arithmetic error.

Such an arithmetic error appears to be a distinct possibility. The correlations involving both *Oocystis lacustris* and *Scenedesmus denticulatus* also improved greatly after removing Clear Lake values from the MLR models, particularly for *S. denticulatus*. Again, reducing the cell densities improved correlations. These findings support the idea that there was an arithmetic error made in the calculation of the original densities from one of the three samples analyzed from this lake. Unfortunately the original count sheets for the particular sample in question were not available for verification.

Although *Ankistrodesmus falcuatus + spiralis* was the second most widely distributed alga (occurring in 18 of the 21 lakes), it lacked significant correlations with most of the independent variables, including all of the primary water chemistry parameters measured in this study (i.e., the conservative water ions and phosphorus). There was weak evidence found for suggesting that vanadium is the key trace metal for explaining the distribution of this species (the OrZnV ratio was the second most significant parameter after ExVCo in all MLR models with ratios in them). The other peculiar fact discovered in this research about *Ankistrodesmus falcuatus + spiralis* was which lakes they were absent from, the two Willamette Valley lakes and Carter. The absences from Clear (Marion Co.) and Carter might be explained on the basis of infrequent sampling, and the absence from Oswego by the addition of copper sulfate. However, the possibility of a single common cause also needs be evaluated, following the principle of Occam's Razor. Airbourne vanadium dust precipitating into these lakes could be the sought-after single cause, but data from this research do not provide clear support for such a hypothesis. Since this is a common and widely distributed taxon, further investigation appears to be required.

Figure 29. Summer densities of *Staurastrum gracile* vs. total sedimentary V (in ppm·dry wt⁻¹).

Figure 30. Summer densities of *S. gracile* vs. total available and organic Cu (in ppm·dry wt⁻¹).

Figure 31. Summer densities of *Selenastrum minutum* vs. organic Cu (in ppm·dry wt⁻¹).

Figure 32. Summer densities of *Oocystis pusilla* vs. organic Cu (in ppm·dry wt⁻¹) and the organic Cu:Co ratio.

Figure 33. Non-zero summer densities of *O. pusilla* vs. total available Cu (in ppm·dry wt⁻¹).

Figure 34. Non-zero summer densities of *Sphaerocystis schröteri* vs. the organic Ni:V ratio.

Figure 35. Summer densities of *Oocystis lacustris* vs. organic Fe (in ppm·dry wt⁻¹).

Figure 36. Summer biovolumes of *Scenedesmus denticulatus* vs. total available Zn (in ppm·dry wt⁻¹).

Figure 37. Non-zero summer densities of *Chlamydomonas* spp. vs. organic Co (in ppm-dry wt⁻¹).

c. Cyanophytes

Cyanophytes were divided into five groups, *Aphanizomenon flos-aquae*, and the bloom-forming and non-bloom-forming species of *Anabaena* and *Anacystis*. Neither *Aphanizomenon* nor the non-bloom-forming *Anabaenas* had any significant findings by themselves as there were too few study lakes with them.

The biovolumes per ml of the bloom-forming species of *Anabaena*, *A. flos-aquae* and *A. circinalis*, were highly correlated with sedimentary organic Ni in all statistical tests performed (Table 8). When all data was included in the MLR model (Figure 38), the adjusted R^2 was 51.0%; for presence data only (Figure 39), the value is 60.0%. In the latter situation the ratio of exchangeable Ni:Mn explained an additional 28.9% of the observed variation. On the other hand, the non-bloom-forming *Anabaenas* did not correlate with organic Ni. Inclusion of them in the relationship caused a reduction in the amount of variation explained between 0.9% and 9.8%.

The primary relationship found between *Anacystis marina* and the independent variables measured was with [Cl]. Except for a possible identification error, no cells of this species were enumerated in any lake with a chloride concentration below 10 mg Cl·l⁻¹. After the [Cl] effect was removed from the regression model for the sole non-nitrogen-fixing bloom-forming cyanophyte in Oregon, it was found to be negatively correlated to the total available Ni in the sediments (Figure 40). The log values of *A. marina* biovolumes were also negatively correlated with a form of sedimentary nickel, exchangeable Ni; though the amount of variability explained was lower (Table 8 and Figure 40).

The non-bloom-forming *Anacystis* species were the only cyanophytes not to correlate with Ni; they were related negatively with total available V (Figure 41).

d. Chrysophytes

All three chrysophytes with significant findings correlated iron, the only phylogenetic division to consistently correlate with a single metal. All values of *Mallomonas* spp. correlated strongest with exchangeable Fe (Figure 42), while non-zero values only correlated best with total available Co (Figure 43). *Chrysococcus rufescens* had a clear correlation with organic Fe and the OrCuV ratio

Figure 38. Summer biovolumes of *Anabaena flos-aquae* and *A. circinalis* vs. organic Ni (in ppm·dry wt⁻¹).

Figure 39. Same as Figure 38, except includes just the presence only data.

Figure 40. Non-zero biovolumes of *Anacystis marina* vs. total available and exchangeable Ni (in ppm·dry wt⁻¹).

Figure 41. Non-zero biovolumes of non-bloom-forming *Anacystis* spp. vs. total available V (in ppm·dry wt⁻¹).

(Table 8). *Kephyrion spiralis* correlated strongest with calcium (Figure 44), followed by organic Fe. The adjusted R^2 values of iron were 44.3% for *Mallo-monas* spp. and exchangeable Fe, 86.9% for *C. rufescens* and organic Fe, and 7.1% for *Kephyrion spiralis* and organic Fe (calcium explained 91.9%).

e. Cryptophytes

Both cryptomonads studied correlated strongly with the mean trophic level index (Figures 45 and 46). Mean TSI explained 31.3% of the variability of *Rhodomonas minuta+lacustris* and 23.3% for *Cryptomonas erosa* (Table 8). There were no cells of *Rhodomonas* spp. found below a mean TSI of 22, nor of *C. erosa* below a TSI of 30.

2. Effects observed upon sedimentary diatoms

The relative abundances in the lake sediments of 46 species of diatoms were examined (species studied are listed in Appendix B.1.); noteworthy findings were found for 38 species. Seventeen species had also been analyzed in the summer phytoplankton populations. Of these 17, six produced the same results as were found in the summer population analyses, seven which lacked positive summer results developed some when their sedimentary remains were assessed (one of these eight, *Cyclotella krammeri*, had a weak summer result which was verified with the sedimentary data), and four revealed different relationships when their relative abundances were analyzed vs. their absolute summer densities. The six species with the same or similar results were *Synedra radians*, *Achnanthes minutissima*, *Nitzschia dissipata*, *N. frustulum*, *Melosira italica*, and *Cyclotella radiosia*; the species observed with differences were *Asterionella formosa*, *Synedra rumpens*, *S. ulna*, and *Cyclotella stelligera*. The uncorrected principal independent variable from five stepwise multiple linear regressions for the 46 species studied are presented in Appendix E.11. The five used were among seven performed (the unused two did not contribute any new understanding(s) to the observed primary relationships). The included MLR models were of all values, of all values where the species was found, of the non-zero values with exchangeable and organic trace metal ratios added to the model, of the same set as before, but including ratios between the different

Figure 42. Summer densities of *Mallomonas* spp. vs. exchangeable Fe (in ppm-dry wt⁻¹).

Figure 43. Non-zero summer densities of *Mallomonas* spp. vs. total available Co (in ppm·dry wt⁻¹).

Figure 44. Non-zero summer densities of *Kephyrion spiralis* vs. water column Ca concentration (in mg·l⁻¹).

Figure 45. Summer densities of *Rhodomonas minuta*+*lacustris* vs. the mean trophic status index and the organic Co:Fe ratio.

Figure 46. Summer densities of *Cryptomonas erosa* vs. the mean trophic status index.

trace metal extractions and nitrogen and phosphorus as well as the N:P ratio itself, and finally, of the presence-only data set with only ratios.

More of the species-specific distribution and abundance are explained by trace metals than can be explained by the standard water chemistry parameters of conservative ions and phosphate or by a trophic level index. Of 89 primary correlations where conservative ions, mean concentration of total dissolved phosphorus, and the mean trophic status index were included in the model, only 33 were related to these factors (Appendix E.11.). Furthermore, 17 of the 33 were either the percent of organic material in the sediments or the percentage of carbonate present. This means that only slightly more than one sixth of the primary correlations observed were due to standard water chemistry parameters; most of the diatom species-specific distributions and abundances correlated better to trace metals.

Of the 38 species with noteworthy correlations, nine species correlated with iron in some form or other, 11 species with manganese (two quite strongly), 14 species with zinc, four species with copper (two mainly due to high Cu concentrations in Crater Lake sediments relative to the amount of nitrogen in the water column), 19 species with cobalt, seven species with nickel, and 13 species with vanadium. The amount of organic material in the sediments and the chloride concentration in the water column were the two most important non-trace metal parameters found in this phase of the research, with correlations with eight and three species, respectively. The regressions of the noteworthy correlations are given in Table 9.

Important findings include the relationships between iron and *Achnanthes linearis* and *Navicula viridula*; Mn and *Achnanthes minutissima*, *A. lanceolata*, *Gomphonema* spp. and *Stephanodiscus transylvanicus*; zinc and *Navicula viridula*, three species of *Melosira*, both species of *Amphora* studied, *Cyclotella radiosa*; Cu and *Gomphonema subclavatum*; Co and the three species of *Melosira*; V and *Fragilaria construens*, *F. pinnata*, *Cocconeis placentula*, and *Cyclotella radiosa*; the percentage of sedimentary organics and *Tabellaria fenestrata*, *Achnanthes minutissima*, both species of *Amphora* studied, and the three common small *Stephanodiscus* species (along with their relationship with sedimentary carbonate concentrations); conductivity and *Cyclostephanos dubius*; and the mean trophic status index with *S. niagarae*.

Table 9. Significant primary regressions for the sedimentary diatom remains.

a. Fragilariales	Equation	Adjusted R ² (in %)
ASFO (presence only)	$= 1.72 + 103. * ExNiFe$	46.6
FRCA (presence only)	$= 19.8 - 1.90 * CoEx$	51.4
FRCA (ratios only)	$= 5.61 + 1.70 * ExVCo$	45.9
FRCN (all)	$= 2.70 + .132 * VOr$	25.5
FRCN (with Big & S.Twin)	$= 0.61 + .288 * VOr$	60.3
FRCN (ratios only, by lake)	$= 6.70 + 5.85 * ExZnMn$	17.2
FRCN (ratios only, by lake)	$= 6.87 + 0.72 + OrVFe$	9.1
[This is the second best parameter.]		
FRPN (presence only)	$= 1.82 + .413 * VEx$	36.5
FRPN (presence only, less Paulina 402 and Walton 305)	$= 0.61 + .502 * VEx$	46.4
FRPN (presence only, with ratios)	$= 13.2 - .147 * ExMnV$	4.4
SNUL (presence by lake)	$= .488 + .234 * Cl$	45.8
SNUL (ratios only, by lake)	$= 1.01 + 9.02 * 10^{-3} * FeExP$	40.6
TBFN (presence by lake)	$= -.397 + .125 * Organic$	17.3
TBFN (presence by lake)	$= 3.34 - .051 * VEx$	18.7 increase
[This is the second best parameter.]		
TBFN (ratios only)	$= 3.27 - .292 * ExVCo$	5.1 increase
[This is the second best parameter, actually a non-linear relationship.]		
b. Eunotiales	Equation	Adjusted R ² (in %)
EUIN	$= -.180 + 1.90 * OrNiCu$	36.9
c. Achnanthes	Equation	Adjusted R ² (in %)
ACLN (presence by lake)	$= 8.10 * 10^{-3} + 9.23 * 10^{-3} * FeExP$	53.7
[Carter values excluded due to possible P measurement error.]		
ACMN (all)	$= 8.55 - .720 * Carbonates$	12.0
ACMN (presence only, with ratios)	$= 7.89 - .232 * \% Organics$	10.9
ACMN (nutrient ratios)	$= .063 + .158 * MnExP$	27.3

Table 9. continued.

ACMN (presence only, with ratios)		
	$= 2.55 - .338 * \text{ExNiCo}$	1.1 (non-linear)
	$= 2.78 - .349 * \text{OrZnCo}$	1.6 (non-linear)
ACLC (presence by lake)	$= 1.43 - .104 * \text{CoOr}$	6.8
ACLC (presence by lake, with ratios)		
	$= .604 + .041 * \text{MnExP}$	25.6
ACLC (ratios only, by lake)	$= .625 + .011 * \text{ExMnCo}$	5.9
ACLC (presence by lake)	$= 1.14 - 1.82 * \text{CoOr/MnEx}$	3.6
COPC (presence only)	$= 4.62 - .011 * \text{VTA}$	15.0
COPC (ratios only, by lake)	$= 1.77 + .087 * \text{MnExP}$	14.3
d. Naviculales		
	Equation	Adjusted R ² (in %)
NVCR (all)	$= -.214 + .126 * \text{Cl}$	15.0
NVCR (nutrient ratios)	$= 0.19 + 13.0 * \text{CoExP}$	52.0
NVCR (presence only, with nutrient ratios)		
	$= 0.41 + 18.4 * \text{CoOrP}$	59.0
NVVR (all)	$= 2.67 - .193 * \text{Sed. Carbonate}$	10.5
PLMC (presence by lake)	$= .098 + .365 * \text{ZnEx}$	43.7
PLMC (presence only, with ratios)		
	$= .039 + 5.34 * \text{ExZnMn}$	67.5
PLMC (ratios only)	$= .337 + 2.68 * 10^{-3} * \text{FeTAP}$	87.5
AFOV (presence by lake)	$= -.309 + .048 * \text{Organic}$	21.7
AFOV (ratios only, by lake)	$= .705 - .057 * \text{OrZnCo}$	5.8 increase
AFPR (presence only)	$= 2.1 - .075 * \text{Organic}$	34.8
AFPR (nutrient ratios)	$= .817 - 41.5 * \text{ZnOrN}$	29.1
CMMN (presence only, with ratios)		
	$= -.202 + .035 * \text{OrMnCo}$	59.6
GFSB (presence by lake)	$= .096 + .028 * \text{CuTA}$	66.6
GFXX (presence by lake)	$= .074 + 7.39 * 10^{-3} * \text{MnEx}$	27.4
GFXX (presence by lake, with ratios)		
	$= .073 + .033 * \text{ExMnCo}$	34.5
GFXX (nutrient ratios)	$= .082 + 1.79 * \text{MnExN}$	44.7

Table 9. continued.

e. Bacillariales	Equation	Adjusted R ² (in %)
EPMU (presence by lake)	$= .243 + 45.2 * \text{NiOrN}$	84.6
EPTR (presence by lake)	$= .825 + .232 * \text{CuEx}$	17.3
EPTR (presence by lake, with ratios)	$= .660 + .718 * \text{ExCuZn}$	27.5
EPTR (nutrient ratios)	$= 1.12 + 2.94 * \text{CuOrN}$	26.9
NZAM (presence by lake, with ratios)	$= .063 + .341 * \text{ExVCo}$	52.1
NZDS (presence only)	$= .460 - .021 * \text{ZnOr}$	27.3
NZDS (presence only, with ratios)	$= .544 - .179 * \text{OrZnCo}$	33.6
NZFR (presence by lake)	$= .502 + .016 * \text{CuTA}$	11.4
NZFR (presence only, with ratios)	$= .636 + .147 * \text{ExVCo}$	15.0
NZGR (presence by lake)	$= -.315 + 3.41 * \text{ExMnFe}$	84.1
NZPC (presence by lake)	$= -.943 + .136 * \text{Organic}$	51.8
NZPC (presence by lake, with ratios)	$= .381 + .048 * \text{ExMnCo}$	37.6
f. Surirellales	Equation	Adjusted R ² (in %)
SULN (all)	$= -.085 + .224 * \text{ZnEx}$	32.8
SULN (presence by lake)	$= -.292 + .324 * \text{ZnEx}$	51.2
SULN (presence only, with ratios)	$= .836 + 1.34 * \text{ExZnV}$	20.2
SULN (nutrient ratios)	$= .739 + .273 * \text{ZnExP}$	84.5
g. Eupodiscales other than the family Thalassiosiraceae	Equation	Adjusted R ² (in %)
MLAM (all)	$= -2.71 + .125 * \text{ZnTA}$	13.9
MLAM (presence only)	$= 39.4 - .747 * \text{CoTA}$	21.5
MLAM (ratios only)	$= 2.65 + 5.15 * \text{OrZnCo}$	19.0
MLAM (presence only)	$= -7.86 + 6.24 * \text{TAZnCo}$	54.6
MLGR (presence only)	$= -2.05 + 1.80 * \text{CoEx}$	31.6

Table 9. continued.

MLIT (presence only)	= 2.20 + .878 * ExVCo	27.0
KSXX (presence by lake)	= .208 + .614 * OrNiCu	45.5

h. Eupodiscales of the family Thalassiosiraceae

	Equation	Adjusted R ² (in %)
CCKR (presence by lake)	= .622 + 32.1 * ExVFe	50.1
CCRD (presence by lake)	= .089 + 0.05 * ZnOr	40.5
CCRD (ratios only)	= .238 + .166 * OrZnCo	25.8
CCRD (ratios only)	= .085 + 3.69 * OrZnV	66.5
CCST (all)	= -.572 + .888 * Cl	42.3
CCST (nutrient ratios)	= 3.28 + 32.9 * CoOrP	49.6
CCMG (presence by lake)	= -1.04 + .543 * Ca	36.3
KYDB (all)	= -.061 + 0.04 * Cl	32.0
KYDB (presence by lake)	= .036 + .039 * VEx	45.9
STHN (presence by lake)	= 2.23 + .333 * Organic	20.3
STHN (all)	= 13.8 - .682 * SedCarbonate	10.4
STHN (nutrient ratios)	= 7.18 + 14.0 * VOrN	20.1
STMN (presence by lake)	= -1.92 + .409 * Organic	12.5
STMN (all)	= 1.05 + .432 * SedCarbonate	10.1
STMN (nutrient ratios)	= 2.36 + .772 * FeOrN	37.1
STTS (all)	= -16.7 + 3.99 * SedCarbonate	53.7
STTS (nutrient ratios)	= 2.54 * MnOrP -.029 * MnOrP	62.3
STNG (presence by lake)	= -10.7 + 3.98 * Mean TSI	22.5
STAL (presence only)	= .288 + .072 * NiOr	16.8

a. Fragilariales

Of the ten species examined from this order of diatoms in the five different MLR models, seven possessed noteworthy findings. The two *Fragilaria* species examined which lacked interesting findings were *F. brevisstrata* and *F. crotonensis*; the latter observation was similar to what was found for this species in the summer phytoplankton. The *Synedra* species lacking interesting findings was *S. rumpens* which had weak summer correlations.

The most noteworthy feature about the variation of the relative sedimentary abundance of *Asterionella formosa* was that the two trace metal extractions which were important in explaining the summer population densities, exchangeable and organic Co, explained less than 1.5% of the variability. The ratio ExNiFe was much more important (Table 9).

The primary independent variable explaining the variability in distribution of relative sedimentary remains of *Fragilaria capucina* was exchangeable Co (Figure 47). When only trace metal ratios were included in the MLR model, then the primary variable was ExVCo (Figure 47). Although these were robust findings, since this species only occurred in the sediments of three lakes, caution is advised in interpreting the results.

The relative abundance of *Fragilaria construens* in lake sediments had the highest correlation with organic V (Figure 48). After the reduced numbers found in both Big and South Twin were removed from the presence-by-lake data (Figure 49), the resulting adjusted R^2 was one of the stronger correlations found for the relative numbers of sedimentary diatoms.

Exchangeable V was the sole important independent parameter which correlated with *Fragilaria pinnata* (Figure 50). If two outliers (Paulina 401 and Walton 305) were removed, the coefficient of determination increases by nearly 10%. When only ratios were included, the amount of variability explained by the primary one, ExMnV, was only 6.0%, about one-sixth of that explained by VEx.

It is noteworthy that the sedimentary V concentration is important for all species of *Fragilaria* which possessed any correlations with the parameters studied here; this finding will be discussed further in the following chapter.

Scatter graphs comparing the relative abundance of *Synedra radians* revealed non-linear, inverse relationships with organic Zn (Figure 51) and the

Figure 47. Relative sedimentary remains of *Fragilaria capucina* (in percent of total composition) vs. exchangeable Co (in ppm·dry wt⁻¹) and the exchangeable V:Co ratio.

Figure 48. Relative sedimentary remains of *Fragilaria construens* (in percent of total composition) vs. organic V (in ppm·dry wt⁻¹)

Figure 49. Relative sedimentary remains of *F. construens* (in percent of total composition) except for Big and South Twin Lakes vs. organic V (in ppm·dry wt⁻¹).

Figure 50. Relative sedimentary remains of *Fragilaria pinnata* (in percent of total composition) vs. exchangeable V (in ppm·dry wt⁻¹).

Figure 51. Relative sedimentary remains of *Synedra radians* (in percent of total composition) vs. organic Zn (in ppm·dry wt⁻¹).

Figure 52. Relative sedimentary remains of *S. radians* (in percent of total composition) vs. the organic Zn:Co ratio.

Figure 53. Relative sedimentary remains of *S. radians* (in percent of total composition) vs. the organic Zn:Fe ratio.

OrZnCo and OrZnFe ratios (Figures 52 and 53). Due to the non-linearity of the relationships, the adjusted R^2 s were low (<15% for ZnOr, lower for the ratios). These correlations were not, however, due to a single outlying lake as the scatter plots demonstrated. These graphs comprise a significant finding to be discussed further in the next chapter.

The best predictor of the relative abundance of *Tabellaria fenestrata* is the percent organic material in sediments (Figure 54). Exchangeable V was the second most important independent variable after organics (Figure 55). When ratios replaced absolute concentrations in the MLR model, ExVCo replaced VEx as the second strongest relationship though it explained only 5.1% of the variation in the relative abundance of *T. fenestrata* (Figure 56) because this species had a non-linear relationship with the ratio.

b. Achnanthes

All four species examined from this order, *Achnanthes lanceolata*, *A. linearis* (Figure 56), *A. minutissima*, and *Cocconeis placentula*, possessed significant correlations with the independent parameters included in these analyses.

Nearly all sedimentary samples had some *Achnanthes minutissima* frustules. The initial MLR model, as well as the non-zero only values (116 of 126 possible) version, yielded a strong relationship between the relative abundance of *A. minutissima* and sedimentary carbonates. However, when trace metal ratios were added to the model, the percentage of sedimentary organic matter replaced the carbonates as the primary, but non-linear, variable (Figure 57). When all ratios were included in the MLR, the ratio MnEx:P became the primary independent variable, though this relationship appeared to be due mostly to high abundances of *A. minutissima* in Loon Lake. The ExNiMn ratio also apparently possessed a strong non-linear, relationship with this diatom (Figure 58), and was the third most independent variable in two MLR models. MnEx by itself, however, did not highly correlate. Both ExNiCo and OrZnCo were also possibly important non-linear relationships for this diatom just as they were for the summer water column abundances. ExNiCo increased in significance after the outliers (Carter and Lake of the Woods 102) were excluded; their inclusion or exclusion did not change the significance level for OrZnCo. Both were mostly caused by high Loon Lake values (Figure 59).

Figure 54. Relative sedimentary remains of *Tabellaria fenestrata* (in percent of total composition) vs. the percent sedimentary organic material.

Figure 55. Relative sedimentary remains of *T. fenestrata* (in percent of total composition) vs. exchangeable V (in ppm·dry wt⁻¹) and the exchangeable V:Co ratio.

Figure 56. Relative sedimentary remains of *Achnanthes linearis* (in percent of total composition) vs. the exchangeable Fe:P ratio.

Figure 57. Relative sedimentary remains of *Achnanthes minutissima* (in percent of total composition) vs. the percent sedimentary organic material.

Figure 58. Relative sedimentary remains of *A. minutissima* (in percent of total composition) vs. the exchangeable Ni:Mn ratio.

Figure 59. Relative sedimentary remains of *A. minutissima* (in percent of total composition) vs. the organic Zn:Co ratio.

The relative abundance of *Achnanthes lanceolata* correlated strongest with organic Co in the sediments when only non-zero values were included in the model (Figure 61). When the nutrient to trace metal ratios were added to the MLR model, the MnEx:P ratio became the strongest parameter (Figure 60), primarily due to Loon Lake. When exchangeable and organic trace metal ratios were added to the model, ExMnCo had been the most predictive variable for *A. lanceolata*. Since this ratio appeared to be an important parameter as well as the concentration of organic Co, the OrMnCo ratio was also plotted as a possibly important parameter. It wasn't; however the ratio of CoOr:MnEx (Figure 61), though non-linear, indicates that these two extractions apparently strongly interact to control the relative abundance of *A. lanceolata*.

Cocconeis placentula had an inverse relationship with total available sedimentary V which explained 15.0% of the variability in its relative abundance. However, this simple description concealed the presence of a peak at 75-80 ppm (Figure 62), demonstrating *C. placentula*'s oligoecious response to V.

c. Naviculales

Frustules of *Navicula cryptocephala* were found in the sediments of only four of the 21 lakes of this study, Carter, Clear, Triangle, and Woahink. Consequently, the independent parameter which most strongly correlated with all values for this species was the chloride concentration. The best predictor of the relative abundance of *N. cryptocephala* within the four lakes was the CoOrP ratio (Figure 63) with an adjusted R^2 of 59.0%.

When all values were analyzed in the initial MLR model, the predominant independent parameter which correlated best with the relative abundance of the common benthic diatom, *Navicula viridula*, was carbonate concentration. However, if Carter Lake is excluded from the scatter plot, a more Gaussian distribution with carbonate appeared (Figure 64). With the addition of trace metal ratios, OrZnFe became the primary relationship (Figure 65). Both organic Zn and the organic Fe:P ratio apparently contributed to this relationship (Figures 66 and 67).

Pinnularia microstauron was most abundant in the sediments (and water column) of Big Lake among the 21 lakes studied. As a result, all of the

Figure 60. Relative sedimentary remains of *Achnanthes lanceolata* (in percent of total composition) vs. organic Co (in ppm·dry wt⁻¹) and the exchangeable Mn:P ratio.

Figure 61. Relative sedimentary remains of *A. lanceolata* (in percent of total composition) vs. the ratio of organic Co to exchangeable Mn.

Figure 62. Relative sedimentary remains of *Cocconeis placentula* (in percent of total composition) vs. total available V (in ppm·dry wt⁻¹).

Figure 63. Relative sedimentary remains of *Navicula cryptocephala* (in percent of total composition) vs. the organic Co:P ratio.

$$NVCR = .412 + 18.386 * CoOrP; R^2 = .608$$

(All values from all lakes where *Navicula cryptocephala* was found.)

- Carter
- △ Clear
- + Triangle
- × Woahink

Figure 64. Relative sedimentary remains of *Navicula viridula* (in percent of total composition) vs. the percent sedimentary carbonates.

Figure 65. Relative sedimentary remains of *N. viridula* (in percent of total composition) vs. the organic Zn:Fe ratio.

Figure 66. Relative sedimentary remains of *N. viridula* (in percent of total composition) vs. organic Zn (in ppm·dry wt⁻¹).

Figure 67. Relative sedimentary remains of *N. viridula* (in percent of total composition) vs. the organic Fe:P ratio.

relationships found were biased towards parameters which were at their most extreme in Big Lake, ZnEx, the ratio ExZnMn, and the nutrient ratio FeTAP (Table 9).

The percent organic material was the primary independent parameter which correlated with the relative abundance of *Amphora ovalis* (Table 9, Figure 68). The second strongest relationship found was the OrZnCo ratio (increase in adjusted $R^2 = 5.8\%$, Figure 69 [which lacks South Twin 420]). *Amphora perpusilla* also correlated strongest with the percentage of organic material in sediments (Figure 70), but the relationship was in the opposite direction to that for *A. ovalis*. Excluding organic material from the analyses produced a primary correlation between *A. perpusilla* frustules and the ZnOr:N ratio (Figure 70). It is noteworthy that both species of *Amphora* negatively correlated with the concentration of sedimentary organic Zn while having opposite responses towards the percentage of organics.

The primary relationship for *Cymbella muelleri* after trace metal ratios were added to the MLR models was with OrMnCo (Table 9). This ratio produced an adjusted R^2 of 59.6%, though it was dominated by Loon Lake. Three of the next four variables in the ratios only model also involved manganese. The four variables (and the increase in R^2 they contributed) were OrMnV (13.1%), MnExP (4.1%), OrZnMn (3.2%), and OrZnCo (6.6%).

Gomphonema subclavatum was relatively abundant in Crater Lake which greatly influenced the MLR results. The primary variable that it was associated with was total available Cu (Figure 71). The primary factor controlling the relative abundance of *Gomphonema* species other than *G. subclavatum* in the study lake sediments appeared to be exchangeable Mn (Figure 72, Table 9). Adding trace metal ratios to the model made ExMnCo the primary independent parameter; adding nutrient ratios made the MnExN ratio the primary variable (Table 9). Loon Lake values may have biased these results.

d. Bacillariales

Seven species from this order, *Epithemia muelleri*, *E. turgida*, *Nitzschia amphibia* (Figure 74), *N. dissipata*, *N. frustulum*, *N. gracilis*, and *N. paleacea* demonstrated significant findings (Table 9).

Figure 68. Relative sedimentary remains of *Amphora ovalis* (in percent of total composition) vs. the percent sedimentary organic material.

Figure 69. Relative sedimentary remains of *A. ovalis* (in percent of total composition) vs. the organic Zn:Co ratio.

Figure 70. Relative sedimentary remains of *Amphora perpusilla* (in percent of total composition) vs. the percent sedimentary organic material and the organic Zn:N ratio.

Figure 71. Relative sedimentary remains of *Gomphonema subclavatum* (in percent of total composition) vs. total available Cu (in ppm·dry wt⁻¹).

Figure 72. Relative sedimentary remains of *Gomphonema* spp. other than *subclavatum* (in percent of total composition) vs. exchangeable Mn (in ppm·dry wt⁻¹).

The relative abundance of *Epithemia muelleri* appears to be partly controlled by the ratio of organic Ni to Co, and nitrogen availability when compared to organic Ni may also be involved (Figure 73). The large number of nulls under the OrNiCo curve and NiOr:N slope indicates that these are not the primary factors however. Only three lakes had this species (Blue, Morgan and Crater) and all of the high values were in Crater.

Epithemia turgida was a more widely distributed species than its co-genitor, although it also reached its greatest relative abundance in Crater Lake. The primary parameter that influenced its distribution was exchangeable Cu, similar to the findings for *Gomphonema subclavatum*. All of its relationships (Table 9) were dominated by the water and sediment chemistry of Crater Lake, so not too much should be made of them.

The relative abundance of the sedimentary remains of *Nitzschia dissipata* is correlated with OrZnCo (Figure 75), similar to the relationship found for summer populations of this species. The primary correlation for the non-zero MLR model of this species was with organic Zn, but in the opposite direction (Figure 75) of the absolute summer densities' relationship.

As was observed with the summer densities of *Nitzschia frustulum*, the relative numbers of the sedimentary remains of this species distributed in a Gaussian curve with respect to alkalinity, though the peak for the relative abundance was lower than that for the absolute densities (Figure 76). The two parameters which best correlated with the relative abundances of this species in the lake sediments were total available Cu and the ExVCo ratio (Figure 77). Which one was the most important and which was second varied depending upon which model version was selected and whether all values from the lakes where it was found were included in the model or just the non-zero values.

Nitzschia gracilis was mainly found in Crater Lake, so the strongest correlations derived from the variability of this species within its sediments. The primary independent parameter was the ratio ExMnFe (Table 9). Suttle also contributed to the ExMnFe correlation as its slope paralleled that for Crater.

The relative abundance of *Nitzschia paleacea* frustules in lake sediments was most strongly correlated with the percentage of organic material present (Figure 78). The ratio ExMnCo was the most important variable in the trace metal ratios version (Figure 78). Both findings were mainly due to Walton.

Figure 73. Relative sedimentary remains of *Epithemia muelleri* (in percent of total composition) vs. the organic Ni:Co and Ni:N ratios.

Figure 74. Relative sedimentary remains of *Nitzschia amphibia* (in percent of total composition) vs. the exchangeable V:Co ratio.

Figure 75. Relative sedimentary remains of *Nitzschia dissipata* (in percent total composition) vs. the organic Zn:Co ratio and organic Zn (in ppm·dry wt⁻¹).

Figure 76. Relative sedimentary remains of *Nitzschia frustulum* (in percent of total composition) vs. alkalinity (in meq·l⁻¹).

Figure 77. Relative sedimentary remains of *N. frustulum* (in percent of total composition) vs. the exchangeable V:Co ratio and total available Cu (in ppm·dry wt⁻¹), non-zero values only.

Figure 78. Relative sedimentary remains of *Nitzschia paleacea* (in percent of total composition) vs. the percent sedimentary organic material and the exchangeable Mn:Co ratio.

e. *Surirellales*

The primary independent parameter correlated with *Surirella linearis* in most of the different models was exchangeable Zn, either by itself or in a ratio (Table 9). This was caused by the relatively high abundance of *S. linearis* in Big Lake, similar to what had been observed for *Pinnularia microstauron*.

f. *Eupodiscales* other than the family *Thalassiosiraceae*

The primary independent parameter for *Melosira ambigua* in the initial version of the MLR model was total available Zn (Figure 79), accounting for 13.9% of the variability. When only the presence data were considered, total available Co replaced ZnTA as the strongest relationship (Figure 79), though the latter remained second in importance in the model for all versions until the final, ratios only, one. The CoTA correlation remained the strongest one (21.5%) until only ratios were considered; the OrZnCo ratio then became the best predictor (Table 9). From these results, it appeared that a new parameter, the ratio of total available zinc to total available cobalt might explain more of the variability of this species than had any of the previous parameters. Over half of the variability of *M. ambigua* (54.6%) was explained by the new parameter (Figure 80), and the high relative abundances from Lake of the Woods were aligned much better with those from the other lakes than previously. One interesting feature of the plot of the new parameter was the separation of the Willamette Valley lakes from the remainder of the study lakes. They formed a distinct, somewhat linear, cluster lying below the rest of the values. Excluding the Willamette values increased the adjusted R^2 for the other lakes to 81.3%.

Exchangeable Co was the only primary parameter to correlated with *Melosira granulata* (Figure 81). CoEx:P replaced it when only ratios were present in the model, but this parameter explained less of the variability (27.8%). Total available Zn was usually the second or third factor for this species.

Unlike the regressions for the summer densities of *Melosira italica*, the relative abundances of its sedimentary remains lacked any relationship to just organic Co and possessed an inverted relationship with the OrVCo ratio (Figure 82). However, the strongest relationship found for this species in lake sediments was still based upon the same two trace metals, though from a

Figure 79. Relative sedimentary remains of *Melosira ambigua* (in percent of total composition) vs. total available Co and Zn (in ppm·dry wt⁻¹).

Figure 80. Relative sedimentary remains of *M. ambigua* (in percent of total composition) vs. the total available Zn:Co ratio.

Figure 81. Relative sedimentary remains of *Melosira granulata* (in percent of total composition) vs. exchangeable Co (in ppm·dry wt⁻¹).

Figure 82. Relative sedimentary remains of *Melosira italica* (in percent of total composition) vs. organic Co (in ppm-dry wt⁻¹) and the organic V:Co ratio.

different extraction, that of the ratio, ExVCo (Table 9). This relationship was positive, just as the one between summer absolute water column *M. italica* densities and OrVCo had been. Again *M. italica* also demonstrated the relative importance of zinc for planktonic *Melosira* as this trace metal appeared in almost all regressions immediately following cobalt, usually either in the organic form or in the ratio ExZnV. Organic Zn explained over 15% of the variability in the non-zero values only version; the ExZnV ratio also explained an additional 15% in the trace metal ratios version after ExVCo; and the ZnOr:P ratio explained nearly 22% more of the variability beyond that explained by ExVCo in the trace metals to nutrient ratios version of the MLR model.

It is noteworthy that these three species of *Melosira* correlate strongly with Co, then with Zn and/or V, but that the fourth species studied from this genus, the semi-benthic *M. distans*, lacked any consistent correlations with any metal. It most strongly correlated with water chemistry, specifically calcium (adjusted $R^2 = 18.7\%$), the amount of sedimentary carbonates, or the N:P ratio, depending upon model version and number of samples included in the analyses.

Frustules of *Coscinodiscus* sp. mainly occurred in the sediment of lakes where the chloride concentration was above $10 \text{ mg}\cdot\text{l}^{-1}$ (Figure 83) as it was almost exclusively found in Carter, Eel, Mercer, and Woahink Lakes. With trace metal ratios in the model, OrNiCu became the predominant factor (Figure 84).

h. Eupodiscales of the family Thalassiosiraceae

Twelve species, belonging to three genera from this family, were found in the sediments of the 21 lakes, eleven in sufficient numbers for statistical analysis. Ten of the 12 had important findings (Table 9).

Cyclotella krammeri (formerly = *C. kützingiana*, Håkansson 1990a, b) was common in only two of the 21 lakes, Blue and Suttle. Blue and Suttle also had the only summer population reports of this species among these lakes. The MLR model of the summer populations suggested a possible, but very weak, relationship between this species and the OrVFe ratio. Once trace metal ratios were added to the MLR model for the sedimentary relative abundances of *C. krammeri*, the primary independent variable found was the ExVFe ratio, and OrVFe was the second best predictor (Figure 85).

Figure 83. Relative sedimentary remains of *Coscinodiscus* sp. (in percent of total composition) vs. water column Cl concentration (in mg·l⁻¹).

Figure 84. Relative sedimentary remains of *Coscinodiscus* sp. (in percent of total composition) vs. the organic Ni:Cu ratio.

Figure 85. Relative sedimentary remains of *Cyclotella krammeri* (in percent of total composition) vs. the exchangeable and organic V:Fe ratios.

Organic Zn remained the strongest independent parameter correlating with *Cyclotella radios*a (formerly = *C. com*ta, Håkansson 1986) through the MLR model version which included all ratios (Table 9). When ratios alone were used in the MLR model, OrZnCo replaced ZnOr but with a lower adjusted R² (Table 9). The primary ratio from the summer correlations, OrCuV, explained 56.3% of the variability after the samples from the East #4 core were dropped from the regression. However, the strongest parameter for the relative abundance of *C. radios*a frustules was OrZnV (Figure 86).

The strongest independent parameter correlating with all values of *Cyclotella stelligera* was the chloride concentration (Figure 87), just as had been the situation for the summer populations of this species. Chloride concentration remained the primary variable until the trace metal to nutrient ratios version of the MLR model. In this version the CoOr:P ratio demonstrated a better fit with the relative abundance of *C. stelligera* (Figure 88). Organic V and the positive summer ratios, OrVCo, ExVCo, and ExCuV, were not strongly correlated with the relative sedimentary abundance of this diatom. Nor was there a relationship found when just the positive summer lakes were analyzed.

Cyclotella meneghiniana apparently prefers harder water than was common among the lakes in this research as it was primarily and positively correlated with dissolved calcium (Table 9). There were no trace metal findings which explained over 10% of the variation of this species.

Cyclostephanos dubius (formerly = *Stephanodiscus dubius*, Round 1982; Theriot, et al. 1987; Theriot, Stoermer and Håkansson 1987) is considered to be typical of eutrophic lakes and/or bodies of water possessing a high conductivity (Anderson 1990, Bailey-Watts 1986). However, when *C. dubius* was plotted against conductivity (Figure 89), a Gaussian response curve appeared. The primary independent parameter predicting relative abundance for this species was chloride concentration (Table 9). When only non-zero values were included in the MLR, the primary independent variable was exchangeable V (Figure 90).

The last genus in this family studied for relationships with trace metals is *Stephanodiscus*. The species of *Stephanodiscus* have been completely revised in the past decade, and only one of Hustedt's forms, *S. hantzschii*, is still regarded to be as a valid species. This research follows the new taxonomy of

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Figure 87. Relative sedimentary remains of *Cyclotella stelligera* (in percent of total composition) vs. water column Cl concentration (in mg·l⁻¹).

Figure 88. Relative sedimentary remains of *C. stelligera* (in percent of total composition) vs. the organic Co:P ratio.

Figure 89. Relative sedimentary remains of *Cyclostephanos dubius* (in percent of total composition) vs. water column conductivity (in $\mu\text{ohms}\cdot\text{cm}^{-1}$).

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Håkansson, Stoermer, and their co-workers (e.g., Håkansson and Locker 1981, Håkansson and Kling 1989, 1990, Theriot and Stoermer 1982, Theriot, Stoermer, and Håkansson 1987). There are basically four common forms in this genus, cells with long perivalvar axes such as *S. binderanus* (not observed in this research), medium to large diameter cells with 12, or fewer, fascicles per 10 μm such as *S. niagarae* and *S. alpinus* (both found), and small cells, either with flat surfaces such as *S. hantzschii*, or with undulate centers such as *S. minutulus* or *S. transylvanicus* (all three were found during this study). A sixth species, *S. parvus* (similar to *S. hantzschii* in appearance), may also occur in Crater Lake (Debacon and McIntire 1991, E.F. Stoermer 1993 personal communication).

The three common little *Stephanodiscus* species all have distinctive distribution patterns with respect to the percent organic material in the sediments and the amount of carbonates present. Both *S. hantzschii* and *S. minutulus* are positively correlated with the percentage of organic material, the primary independent parameter for both species (Figures 91 and 92) while *S. transylvanicus* possesses a Gaussian optimum with respect to the percent of organic material (Figure 93). The second most important factor correlated with all three species is the concentration of sedimentary carbonates. *S. hantzschii* has a weak negative correlation negatively with this parameter (Figure 91); the correlation for *S. minutulus* is positive, but weak (Figure 92); while the correlation for *S. transylvanicus* is strongly positive (Figure 93).

When only trace metal ratios and trace metal to nutrient ratios are considered for these three species, the most important parameter is unique for each. For *S. hantzschii*, the primary parameter is the ratio VOr:N (Figure 94). For *S. minutulus*, it is the FeOr:N ratio (Figure 95), though this is largely due to high values from Eel Lake. The ratio MnOr:P is the key trace metal parameter for *S. transylvanicus*, mostly due to the Newberry Caldera lakes (Figure 96).

The fourth small *Stephanodiscus*, *S. parvus*, lacked any significant correlations by itself because it was found almost exclusively in just Crater Lake. This was unfortunate as there was some question as to whether or not this population was truly *S. parvus*, or merely a tiny form of *S. hantzschii* (C.D. McIntire 1992 and E.F. Stoermer 1993 personal communications). To test for this possibility, the "*S. parvus*" population was combined with the *S. hantzschii*

Figure 91. Relative sedimentary remains of *Stephanodiscus hantzschii* (in percent of total composition) vs. the percent sedimentary organic material and the percent sedimentary carbonates.

Figure 92. Relative sedimentary remains of *Stephanodiscus minutulus* (in percent of total composition) vs. the percent sedimentary organic material and the percent sedimentary carbonates.

Figure 93. Relative sedimentary remains of *Stephanodiscus transylvanicus* (in percent of total composition) vs. the percent sedimentary organic material and the percent sedimentary carbonates.

Figure 94. Relative sedimentary remains of *S. hantzschii* (in percent of total composition) vs. the organic V:N ratio.

Figure 95. Relative sedimentary remains of *S. minutulus* (in percent of total composition) vs. the organic Fe:N ratio.

Figure 96. Relative sedimentary remains of *S. transylvanicus* (in percent of total composition) vs. the organic Mn:P ratio, identified by lake.

data and the three primary regressions run again. The unadjusted R^2 value for the percent organic material was reduced from 25.7% to 18.1%, as was the R^2 for the relationship with the VOr:N ratio from 21.5% to 16.9%. There was a slight improvement for the sedimentary carbonate relationship from 6.7% to 8.0%. The overall change, however, was for the worse, suggesting that the observed "*S. parvus*" population is distinct from *S. hantzschii*.

Both *S. niagarae* and *S. alpinus*, the two large species of *Stephanodiscus* present in this study, tended to increase in percent composition in the sediments as the mean trophic status index increased; however, the mean TSI explained more of the variability in the non-zero values of *S. niagarae* (Figure 97) than did this parameter for *S. alpinus*. The best trace metal parameter for explaining the variability of *S. niagarae* was the NiOr:N ratio, which was non-linearly correlated with *S. niagarae* (Figure 97). A similar relationship with an organic Ni ratio, OrNiMn, was found for *S. alpinus* (Figure 98).

The relative abundance of the non-zero values of *S. alpinus* correlated best with organic Ni (Table 9), though this relationship was weaker than the one involving OrNiMn. Since *S. niagarae* correlated with the NiOr:N ratio and *S. alpinus* correlated directly with NiOr, a graph of *S. niagarae* vs. organic Ni was also plotted. This plot revealed a weak Gaussian distribution of *S. niagarae* to organic Ni with a peak relative abundance of about 6 ppm.

One last observation about the MLR results correlating individual species of primary producers with the different trace metals, extractions, and ratios should be made. Not once was water column Mo concentration the primary parameter. The highest it ever appeared was fourth in the MLR using all values of summer phytoplankton, and only then because it was part of a unique set of parameters which varied together. Other than that one situation, its frequency of occurrence was probably the lowest for all of the parameters included in all of the different MLR models. It appeared less than 10 times in all 11 MLR versions, other than in that one case, for a maximum frequency of appearance of only 0.2%.

Figure 97. Relative sedimentary remains of *Stephanodiscus niagarae* (in percent of total composition) vs. the mean trophic status index and the organic Ni:N ratio.

Figure 98. Relative sedimentary remains of *Stephanodiscus alpinus* (in percent of total composition) vs. the organic Ni:Mn ratio.

IV. Discussion

A. Methodological Problems and Comparisons

1. Validity of Using Single Station Cores to Describe Entire Lake Processes

An important issue associated with paleolimnological studies is quantifying the amount of variability and errors resulting from sediment coring and analyses. Frequently asked questions include: “What error is associated with the subsampling, processing, and analysis of sediment? How well does a single sediment core represent an entire lake? How accurate are inferences of limnological characteristics inferred from calibration data sets based on surface sediment samples? More generally, what are the sources of variability in paleolimnological studies, and how important are they? (p. 268, Charles, et al. 1991)”

Charles, et al. (1991) examined the diatom and chrysophyte microflora of Big Moose Lake, NY from multiple stations, depths, and subsamples; used this data set to make inferences about the pH changes in this lake over time; then compared the results of their analyses to the known changes and a set of alternatives which could be used to explain the observed variability. In terms of organismal remains in sediments, they concluded that “(o)verall, the variability associated with subsampling, sample preparation, and counting are negligible (p. 271).” Diatom and chrysophyte “(a)ssemblage composition appears to be affected by factors such as depth, distance from shore, and sediment accumulation rate (p. 272).” Paleolimnological variability was found by these authors to be “related primarily to differences in contributions from source areas or differences in the time periods represented, the latter being a function of variability in sedimentation and mixing rates throughout the lake (p. 279).”

These authors concluded, based upon their research, “that a single sediment core can adequately represent the overall trends (in terms of historical water chemistry changes, [at least for pH - Comment added by AHV]) that have occurred in a lake (p. 268).” This investigation used samples from multiple depths of replicate cores in all lakes studied, thus three of these four frequently asked paleolimnological/sedimentology questions about the general scientific validity of the conclusions derived from measurements such as these can be answered affirmatively for this study.

Furthermore, while variability is an important phenomenon in lake sediments, Charles, et al. (1991) demonstrated that most of the variability

present can be explained by known factors, if these are known from either historical records or through an understanding of ongoing physical, chemical, and biological processes in the lake. Thus, most of the variability observed in this research should be due to a known cause or through a mechanism which could be readily explained.

This leaves only the question of the accuracy of inferences of limnological characteristics based upon sedimentary samples. Both the relationships between water chemistry and sediments and those which control the sedimentation of small biological remains are known at least on a general basis, if not in great detail, as documented in the Literature Review of this dissertation. The sole conceptual question remaining is how robust is the inferred linkage between water column biology and sedimentary trace metal chemistry. Based upon the results of this research viewed as a whole, the answer to this last question appears to be that it varies depending upon both the metal and biological species under consideration, and that there is no single answer for such a question. Some results, such as the frequently observed correlations between sedimentary zinc and diatoms, suggest clear, specific linkages. Other results, such as the infrequent links between exchangeable Mn and any species of algae, the rare positive correlations between sedimentary Cu and diatoms, or the even clearer absence of correlations between sedimentary diatom remains and water column Mo concentrations, indicate that these three trace metals have either limited, or no links with the primary producers.

2. The Problem of Contamination and Attempts to Correct for It

a. Field

Metal contamination is a serious problem both in the field and in the laboratory. Collier and Edmond (1981) have pointed out a number of possible field sources including, but not restricted to, paint particles and/or rust flakes off of the sampling platform or boat, leaching or particulate (i.e., scale) losses from both the sampling device and the sample storage container, and atmospheric pollution of the sample during the sampling period.

The problem of vessel contamination was completely avoided here by using either unpainted aluminum skiffs or a fiberglass boat painted white with either a chromium-based or marine latex paint. No paint particles were ever

found in the cores. The sampler and sample storage container were essentially the same piece of Lexan™ plastic tubing, a non-metallic material. The only other parts of the sample storage equipment were two black rubber stoppers, again non-metallic in nature, and duct tape, used only on the outside of the stoppers and plastic tubes to seal them shut. Finally, most of the lakes are located in rural settings, or in the case of Lake Oswego, were sampled on days lacking serious air quality problems. Consequently, airborne pollutants should have been no worse than the general background level.

The sole possible field source of metal pollution for these cores was the coring device itself. The frame and external ring clamp were made of a high quality steel, the weights surrounding the opening of the corer were lead, and the pressure-release valve was composed of two hard plastic disks similar to Plexiglass, a black rubber gasket between them, and a bronze or brass nut attaching the valve to the central steel rod. Neither the frame nor the weights made direct contact with the core liner nor with the exact area of sediment being sampled. Furthermore, unlike in the ocean where corrosion of steel parts is a serious source of potential contamination, no evidence of any rust or corrosion was observed, even after several years of use. Moreover, except for trace contaminants by the metals of interest in the lead, the weights themselves should not have been a source of contamination. The external ring clamp never made contact with the inside of the Lexan tubing and it was composed of stainless steel. I used the same make of ring clamps in oceanographic work for a number of years, and have observed that it takes a long period of repeated exposure to salt water without washing combined with hard use before these stainless steel clamps begin to corrode. For these reasons, the ring clamp was considered to be a highly unlikely source of contamination.

Thus the only possible location within the coring device where trace metals might have been introduced into the cores was the brass or bronze nut holding the pressure-release valve. Both bronze and brass, specially the latter, are widely used in the marine environment because they resist corrosion, thus the probability of the nut contaminated the cores was judged to be extremely low. Moreover, the only metals of interest which could have been added were copper and zinc.

Given the field sampling protocols and type of corer used, it seems highly probable that no significant metal contamination occurred during the core collection.

b. Samples in the Lab

Avoidance of contamination in the laboratory was less successfully achieved as errors found during the data reduction demonstrated, despite the use of ultra-clean techniques and high purity reagents. There were three main sources, airborne particles settling in the beakers during the extractions, acid-resistant organic films on the insides of the volumetric flasks which carried trace metals from one use of the flask to the next one, and the difficulties caused by doing this research in a non-trace-metal-clean lab.

Both Van Loon (1982) and Collier (personal communications) recommend using positive pressure laminar flow hoods over the older exhaust hood used here for avoiding external contamination. Urban particulate matter apparently is quite high in zinc (Collier personal communication and personal experience); hundredfold increases in exchangeable and HCl-extracted zinc were occasionally found due to these particles. (Interestingly enough, the organic fraction from the contaminated samples did not have such increases, providing support for Tessier's claim (Tessier and Campbell 1988, 1991) that these are selective extractions.) On at least two occasions there were also backblows from the exhaust hood which produced visible soot particles on the surface of the solution being extracted. A partly successful attempt was made to reduce this as a contamination source by covering the beakers before leaving the work area.

The problem of acid-resistant organic films on the inside of some of the volumetric flasks was discovered part way through the lab work when a subset of the same volumetric flasks were observed to repeatedly have higher than expected concentrations between different cores. All flasks were then treated to a detergent prewash with three extra rinses of Nanopure™ before the standard acid wash and seven Nanopure™ rinse treatment. After a second detergent prewash treatment, the problems disappeared. Between seven and twelve flasks, depending upon the metal and severity of the problem, had detectable amounts of film-caused contamination. The trace metal values

from those flasks before the detergent washes were excluded from the statistical analyses.

It proved to be impossible to follow one of Van Loon's (1982), Collier's and Roe's (personal communications) cleanliness procedures to be followed in a "trace-metal-dirty" lab setting for avoiding trace metal contamination, namely, to keep an area of the lab trace metal clean and reserved for trace metal work only. Although airborne particulates and the film problem were more serious sources of error, on at least three occasions, large portions of individual extractions were lost due to violations of this procedure. All of the known contaminations from this source have also been excluded from the final analyses.

While splattering, a fourth major source of potential contamination, occasionally occurred during the heated extractions, the extent to which it influenced the final results was minimized by only analyzing a single lake at a time. Also by using replicates from within each lake, any serious variability could be spotted during the data reduction. Of the total of 438 measurements for each unique core-depth-extraction, the results of less than 10 (a maximum error rate of less than 2.3%) indicated potential splattering problems. The clearest example of this problem was the Morgan 120 oxide extraction.

The loss of replicates due to contamination in the lab mainly just reduced the statistical confidence of the final results, but except for a few zinc extractions, all produced measurable values. The reduction in statistical confidence was worrisome mainly because four of the seven metals were close to their detection limits in two of the extractions (exchangeable and peroxide forms of Zn, Cu, Co, and Ni) as was a fifth (V) upon occasion. Unfortunately in a few situations, the number of surviving replicates was extremely low, particularly for Paulina; and in still fewer situations, the average matrix effect for a specific trace metal from other samples in the same core or from the same lake had to be used instead of a core-depth-extraction specific matrix. The trace metals which suffered the greatest loss of statistical confidence due to the loss of replicates were cobalt and vanadium. For the low matrix effect metals, manganese, copper, and nickel, this was not a source of error as these metals tended to have the same matrix effect by extraction even between lakes, especially copper (its matrix effect was almost nil). The only problem the loss of replicates

caused for the analysis of zinc was that sometimes the remaining samples had a high enough concentration to be slightly above the linear range of AAS response; fortunately the matrix variability between samples from within the same core was quite small for this metal. Contamination of the entire extraction was much more of a problem for this metal than individual replicate flask contamination. Iron, which has a very high matrix effect, was always present in large enough concentrations for the loss of a few individual replicate flask values not to be a problem.

c. Statistical Treatment of Contamination Errors

The trace metal concentrations derived from the AAS analyses were determined through the procedure of Standard Additions. This technique generated the concentration and its standard deviation through the construction of a linear regression equation. The equation initially used all individual replicates of each sample. However, early during the data reduction, a number of replicate flasks with erroneous values were discovered. In order to obtain more accurate measurements from among the numerous replicates analyzed, a thorough and efficient method for identifying replicate errors was a necessity. The method developed is discussed here.

The problem of individual volumetric flask contamination is a separate class of analytical difficulty from the contamination of an entire sample discussed previously, although the cause was typically also the trace-metal-dirty lab. Replicate errors were anticipated because of the difficulties in maintaining a "clean" environment, although a serious attempt had been made to minimize them by keeping the flasks stoppered. Pigmented chalk dust was unfortunately abundant in the lab, usually invisible to the unaided eye, and several of the pigments appeared to be trace metal based. Frequently it appeared that just a few particles falling into a volumetric flask were adequate to cause a high value for one or more, but not all, trace metals from that replicate, the usual pattern observed. While urban dryfall during individual extractions was also a possible cause, contamination due to it usually tended to produce very high concentrations of zinc and/or vanadium in all replicates, not the small shifts observed in the individual replicate flasks.

A statistical characteristic of the distribution of a large set of values resulting from any analytical chemistry technique is that as the concentration approaches the detection limit, the amount of variability in the estimate of the concentration increases (Kolthoff, et al. 1969). In an analytically error-free universe, a pattern much as is shown in Figure 99 should be expected. This characteristic was used to develop the described method for quickly detecting samples which possessed one or more deviant replicates.

Using the mean value and standard deviation generated by the SA linear regression for the concentration, the standard error of the mean, expressed as a percentage of the mean, was calculated for each specific metal-extraction by core identity. For example, the unadjusted percent standard error for the peroxide-extracted manganese from Blue Lake core #4 at 5 cm was 7.1% while for MnOr in Blue 402 it was 117.4%, and so forth. Next, the percent standard error for a specific sample and metal was plotted against the log of the mean concentration of that metal in that sample, using all of the samples collected from four to seven lakes as a composite data set. (The log of the mean concentration was used instead of the absolute concentration for clarity.) Values with erroneous replicates appeared above the slope of the curve.

After identification of the particular sample that had a “bad” replicate (or replicates), the linear regression for that sample is plotted so that the “bad” replicate might be identified. The replicate which decreased the regression coefficient by the greatest amount is the one removed. Finally the data set being studied is re-plotted to include the new percent standard error and mean. This process is repeated as necessary to a minimum of three replicates per sample (That small a number of replicates was extremely rare; less than 8 such metal-extraction-samples were encountered during the entire study). The latter part of this “error detection by internal variability” technique, the deletion of influential cases which bias results, is part of a standard statistical method known as the *Studentized deleted residual* (Norusis 1990). The procedure is a version of Cook’s Distance used for measuring the effectiveness of the deletion. The only unique feature of this new statistical technique is the application of residual measures to plots of variability vs. concentration.

Individual flask contamination was not the only source of analytical error found during the data reduction phase. A less common replicate error, an

Figure 99. An example of the increased variability with decreased sample concentration.

incorrect auto-pipette addition also occurred. This class of replicate errors was easy to detect and correct for, as all of the metals in an individual volumetric flask were either lower or higher than the slope or the duplicate addition, and the amount that they were off was constant from metal to metal. The mean difference for all seven metals was used as a correction term and the values were retained from all flasks that exhibited such errors.

3. Variations in the Extraction Procedure and Replicates

There are numerous difficulties with selective and/or sequential chemical extraction procedures (Calmano and Förstner 1983, Rapin, et al. 1986, Tipping, et al. 1985,); however, the utility of such methodology for providing insight into bioavailability of trace and heavy metals is enormous (Di Toro, et al. 1992, Morrison, et al. 1986, Samanidou and Fytianos 1987, Tessier, et al. 1984, Tessier and Campbell 1987). Consequently, this approach has developed a considerable amount of interest and much discussion about its accuracy and selectivity (Belzile, et al. 1989, Nirel and Morel 1990, Tessier and Campbell 1991), and several techniques have been developed to reduce analytical error in these extractions (Belzile, et al. 1989, Rapin, et al. 1986). Such techniques have been of considerable use during the analysis of the cores from this research as not all of them were processed the same way.

A major source of variability between cores was the condition of their storage. Rapin, et al. (1986) determined that the best way to store sediment cores in order to keep the trace metal components in their original fractions was to keep them in the original wet form and refrigerated at about 4 °C; drying especially caused transformations. Unfortunately a number of cores were dried and analyzed by AAS before learning of this procedural improvement. Also, due to a refrigeration failure, a number of cores were “cooked” at over 30 °C for about six weeks before being discovered. “Cooked” cores from two lakes were analyzed instead of resampling those lakes because one (Squaw) possesses very severe logistical problems for sampling (“cooked” cores from both Bolan and Wallowa were retained for the same reason) and the importance of the other lake (Lava) was not realized until near the conclusion of the chemical extractions.

Eight dried cores were analyzed, Carter #1, Clear #1, Big #1 and #3, and the cores from Lake of the Woods and Triangle. Results from three of the eight dried cores, Clear #1, Big #1, and Big #3, were not used in this research, except to compare station differences in Big Lake and the types of changes that drying produced. The information gained from the latter analysis was used to evaluate the results from the other five cores.

Drying appears to shift Fe from the exchangeable fraction to the HCl-extracted fraction while increasing the Mn and Cu concentration in the exchangeable fraction (Rapin, et al. 1986). These patterns were also observed for Fe in Big #1 and Carter #1, and for Mn in Carter and Clear, though not in Big. Exchangeable Cu did not increase in the lakes of this study. There were neither significant changes in the organic fractions of these three metals in any of the cores, nor were there any consistent changes by Zn, Co, Ni, and V from any fraction analyzed in this study. The former fact suggests that the organic extraction was more stable than either the exchangeable or oxide ones. The latter finding suggested that changes due to drying were metal-specific.

While cooking clearly altered the distribution of some trace metals from some of the extractions, there was no consistent pattern found for either the exchangeable or organic extractions as revealed by a comparison between the cooked and non-cooked cores from Big and Suttle Lakes (Appendix A). Furthermore, when the concentrations of all seven metals were plotted against two indicators of biological productivity, Secchi Disk depth and concentration of chlorophyll *a*, there were no consistent separation shown between the cooked and non-cooked cores. The only differences observed were due to a single erroneous value, unequal sample size, or a combination of these two factors. This suggests, but does not prove, that increased biological activity at the higher temperatures may not have been a serious problem in this study. Unfortunately, parameters which might have given a direct measure of the amount of microbial activity and/or concentration of bacteria present were not taken.

Significant readsorption due the sequential extraction process has long been considered to be a potentially very serious problem with this procedure (Belzile, et al. 1989). Belzile, et al.(1989) documented that much of the concern previously expressed is due either to the size of the spike added in past studies

or to the use of model sediments. The use of model vs. natural sediments is very bad in this respect as apparently newly combined material is not in thermodynamic equilibrium while some combinations used, such as amorphous Fe oxide and Fe sulfide, do not co-exist in the natural environment which consequently can produce some rather large and rapid changes (Belzile, et al. 1989). The addition of large spikes relative to the background concentrations has the effect of overloading the absorption capacity of the different components of natural sediments, which then permits re-distribution of the excess. The results of Belzile, et al. (1989) thus suggested that unless large amounts of reactants are added, or the kinetics of the chemical reactions are significantly faster than the original total of 6-24 hours of reaction time (Tessier, et al. 1979), that sequential extraction should provide relatively accurate, and reproducible, results.

Oxygenation of anoxic sediments during stirring was the only process which could fit the size criteria of quantity of reactants and length of time to produce significant sediment transformations (Belzile, et al. 1989). Oxygenation of sediments will cause a shift from metal sulfides to metal oxides and from exchangeable iron to the iron oxide fraction (Rapin, et al. 1986). Anoxic sediments were not typically found above 3-6 cm in this study nor were they found any shallower by either Belzile, et al. (1989) or Vesel'ý, et al. (1993). The 20 cm depth, however, was apparently always anoxic, so would have been strongly affected by oxygenation during stirring.

By reducing the amount of sulfides extracted by the hot peroxide treatment, oxidation of sediments during the exchangeable extraction greatly increases the likelihood that only organic material was analyzed by the hot peroxide extraction in most of the lakes (East and Todd being two significant exceptions) and explains why there was so little extra Zn in the hot peroxide extraction from Squaw Lake. It also suggests that the exchangeable Fe measured here was probably seriously underestimated. (Because of slower oxidation rates and/or lower concentrations, the other six trace metals measured were not considered to have as significant a loss as iron, if any, other than for zinc in Squaw Lake.) However, since the concentration of exchangeable Fe varied by two orders of magnitude (from over 3000 ppm in Todd and the Coastal lakes except Carter to around 50 ppm in Blue and East Lakes), it is likely

that the observed FeEx differences have some basis in reality. That is to say, the losses from the exchangeable and sulfide iron pools to the oxide pool are probably proportional to the amounts in the original pools.

A different line of evidence also suggested that the hot peroxide extraction liberated almost exclusively trace metals associated with organic material of a biological origin. The results of the first set of two-way ANOVAs between lake trophic status indices and the 21 different trace metal extractions yielded only eight important correlations between any trophic status index and trace metals. However, four of the eight were with an organic extraction, Co, Mn, Ni, and V, and two more (CoTA and MnTA) also included the organic extraction. These six included all five significant correlations with chlorophyll α , a direct estimator of biological standing stock, while the remaining two were with tdp only, which is only an indirect measure. The strength of these ANOVAs is demonstrated by the fact that none of them were adjusted for the presence of any sulfur springs in a particular lake, i.e., all of the lakes were lumped together as is.

Initially two different techniques were used to extract trace metals present in the residual fraction, ashing at 550 °C and wet ashing with perchloric acid. Seventy-two percent of the time the perchloric ashing gave significantly lower results than did the dry ashing. Since the dry ashing procedure was performed in a closed furnace which did not allow particulate matter to be added to the sample, and the inside of the furnace did not produce material itself, the observed difference required resolution. Having ruled out contamination of the ashed material as a source of error, the only possible direct alternative for the difference was a loss of trace metals in the perchlorate digestion. Since the heating of the residue was very low for both variations of this extraction to protect the rather expensive teflon beakers used and none of the products of this digestion other than silicon hexafluoride were known to be volatile with the exception of the unmeasured arsenic and selenium compounds, significant losses in the perchloric acid version of the residual extraction were considered to be highly unlikely. Therefore, the question became what indirect means were causing this difference. The solution to this concern was found in a re-examination of the procedures used. After dry ashing the samples are re-weighed before HF digestion, then adjusted for the weight of material lost, while there was no

re-weighing of the perchloric digested samples. If the material being removed in both variations of this extraction lacked trace metals entirely, or nearly so, then the difference in the concentrations can be attributed primarily to the correction used in the dry ashing to adjust for the amount of material lost. The concentrations from the dry ashing residual are those of just the silicate matrix, while the concentrations measured with the perchloric acid digestion are from the silicate plus an unknown material which apparently lacked trace metals. As sulfides, carbonates, and the oxide group of compounds had already been removed by the hot peroxide and HCl extractions and heating to 550 °C does not remove the water of hydration from clays (Dean 1974), but heating to 550 ° does ash all organic material not previously digested by peroxide, this suggests that the unknown material is probably a class of peroxide-refractory organic compounds which lacked trace metals.

Because the hot peroxide only procedure used here for digesting organic material did not completely digest all organics as demonstrated by the differences between the perchloric acid vs. dry ashing techniques, there was some question as to whether or not a better procedure for distinguishing between organic trace metals and those of other fractions could be developed. The original extraction procedure of Tessier, et al. (1979) for organic + sulfidic trace metals called for acidification of the samples to a pH of 2.0. This modification was tested using a single replicate core from Triangle Lake. As documented in the Appendix., this experiment liberated nearly half of the oxide fraction as well as the quantity of trace metals that the hot peroxide treatment normally produced. Acidification of the peroxide extraction was not repeated as a consequence of this experiment. Part of the difference in results between the method used here as opposed to Tessier, et al.'s was the sequence of operations. Their method called for first liberating carbonates with 1M sodium acetate, then the oxides with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc before extracting the organics + sulfides with hot peroxide adjusted to a pH of 2.0. The method used here extracted the organics (+ any remaining sulfides) with just hot peroxide before extracting the oxides + carbonates with hot HCl. The sequence of Tessier, et al. enabled a finer resolution of the carbonates and oxides fractions, and by gently removing them first, permits a harsher extraction treatment for the organics. Because the organic trace metals available for, or derived from, biological activity were

of more interest in this research, an earlier, and gentler, i.e., more likely to be more specific, extraction was desired here. Since no other specific techniques for measuring only “organic” trace metals were encountered during the literature review and since the differences in the two residual treatments suggested that the refractory organics lacked large amounts of trace metals as well as probably not being available for most, if not all, biological activity, the original methodology of this research was retained unaltered. As a consequence, the hot peroxide treatment following the initial mixing with MgCl_2 can be conceptually thought of as yielding primarily the biologically derived and available trace metals combined with some of the less easily oxidized sulfides.

Sample replication was obtained either through a comparison between the pairs of cores used from the same lake, or between cores from the same station which were subjected to different extraction and storage procedures, or by replicate volumetric flasks which measured internal sample variability. Replicates, in the sense of split samples from the same core-depth-extraction combination, were done for only INAA totals from Woahink Lake, although the same replication procedure was also done for the AAS analysis to measure the difference between the two Triangle Lake organic extractions. The high time cost of AAS analysis unfortunately made such combinations of methodological tests essential in this research, hence pure within-sample splits were not performed. Based upon the work by Tessier, et al. (1979), Rapin, et al. (1986), and Belzile, et al. (1989), the size of such variability was equal to, or smaller than, that of between replicate cores at the same depth. The latter situation, i.e., smaller than the between-core variability, was the more typical finding of these authors.

Intra-run INAA variability on the same GeLi-detector was less than 10%; however, larger differences in total concentrations for several of the metals were found between both the two software programs and the two different detectors used at PSU and OSU. The concentration differences resulting from the different software seem to have been caused by inclusion of variable “wing” sizes in the version of the PSU program used as such an inclusion was absent from the OSU program. Differences between the two GeLi detectors might also have been due to different sensitivities, but this is purely speculation.

A larger source of concern than within sample variability was the relative lack of comparability between the INAA and AAS results from the 5 cm depths of the Woahink and Eel Lake cores. The origin of these discrepancies was not discovered, and it remains a very worrisome problem. The presence of the strong sand dilution profile in the Woahink station #2 INAA cores which was suggested at using AAS argues against differences between cores being the primary cause for the lack of comparability, but this was the only possible cause for these differences which was eliminated. Further work to calibrate these two analytical methods is recommended.

4. Weaknesses in the Actual Sampling Pattern

The laboratory analyses were halted, due to a time shortage, before measuring all of the lakes that cores had been collected from or of interest. The only ecoregions that had an adequately number of lakes analyzed were the Coastal and Cascades with 6 and 7 lakes, respectively. The remaining four ecoregions had a total of only 8 lakes sampled between them. Consequently, the ecoregion conclusions, other than between the Coastal and Cascades lakes, are weak. While the reductionistic approach initially followed was better fulfilled by the analyzed lakes, there were still inadequate numbers for one of the four water chemistry classes, that of the soft water, high alkalinity lakes, and one of the three trophic level groupings, oligotrophic with high P (In both situations only 3 lakes were analyzed). The two climatic regimes sampled had 8 and 12 lakes (this regards the Klamath-Siskiyou as distinctive in their climatic characteristics), while there were 9 oligotrophic, or oligotrophic to mesotrophic, lakes vs. 7 lakes varying from hypereutrophic to mesotrophic tending towards the eutrophic. However, there were serious problems separating the influences of the different factors; for example, all three soft water, high alkalinity lakes were in the Montane climatic regime while all four high conductivity lakes but only two of the eight soft water, low alkalinity lakes were in the Maritime climatic regime.

5. Limitations upon the Conclusions Due to the General Approach Used

Before discussing the biological results, it is first necessary to clearly define the limits of this research; that is to say, to differentiate between what

this effort can address and what is beyond its capabilities to predict. Because of the sort of questions asked, certain criteria used in experimental research are invalid measures for evaluating any conclusions discussed herein. There is a fundamental difference between experimental and descriptive science. Experimental science manipulates a controlled system and records the results of the experiment(s), while observational science is limited to comparisons, contrasts, and descriptions of *apparently* sequential actions. Despite the relatively sophisticated, and extremely time-consuming, technologies utilized in this research; it is, nonetheless, strictly an observational, or descriptive, study. Hence, causality is, herein, solely inferential.

Consequently, all of the conclusions reached here should be regarded solely as detailed observations awaiting experimental verification from the lab or through field manipulations. Indeed, this was one of the basic objectives of this research as originally formulated; namely to develop a list of potentially important trace metal interactions, by species, from all of the possibilities that have been proposed in other studies. Thus, the results of this research can best be viewed as an initial screening of a host of possibilities; subsequent investigation is required to confirm all findings.

It must be stressed that the observations emphasized in this chapter have been chosen at least partially on a subjective basis. There were however three objective selection criteria used. The first one was the relative significance of a particular species in a range of lakes, i.e., patterns affecting common and widely-distributed species were of greater interest than those that only influenced the distribution of scarce species. The second criterion was the strength of the correlation; was there a clear pattern present, or was the correlation caused by a single outlying lake. The third basis for selection was whether the pattern resembled those previously known from the literature. These criteria are discussed in more detail in the following section.

6. Statistical Analyses

a. Theoretical Limitations to the Trace Metal-Species Approach Used

There are several serious limitations to this approach. The first limitation is simply the one that not all possible physical parameters or trace metal ratios which could affect the distribution of the species under assessment could

be included. As was pointed out in the Introduction, there are a number of important factors, such as light, temperature, nutrients, and predation, which determine much of the distribution and abundance of planktonic organisms. None of the major controlling factors other than phosphorus were examined here. This limitation is caused by several factors; one, not every single possible parameter could be measured due to physical, financial, and/or temporal considerations; two, the number of independent variables which can be simultaneously analyzed is limited to the number of cases (21 for the summer phytoplankton, 126 for the sedimentary diatoms). Just the number of possible trace metal ratios alone is 21 factorial, far larger than the number of cases. A third factor was that the statistical software packages used couldn't handle the data set if too many variables were used at a time.

An attempt was made to at least partly solve the first limitation by making between four and seven MLR runs on each species using different (but standardized) subsets of independent variables which were hypothesized as possibly affecting the species being considered. If the same trace metal or ratio was consistently found to be the “primary” one across these different subsets, then it was regarded as being a relatively robust finding. If not, then the species of algae under examination was considered to not be strongly influenced by different trace metal concentrations or ratios, i.e., it was relatively insensitive. This solution however is rather weak because it is based upon a relatively small number of different MLR runs for each species. The relatively low number of MLR runs was due to the large number of different species examined (38 and 46 for the summer phytoplankton and sedimentary diatoms, respectively).

However, it also should be noted that the purpose of this study was to identify possible factors which explain the variability not already explained by the major factors in the equilibrium model. This research is not an attempt to provide a set of universal, species-specific, mechanisms to explain all distribution and abundance patterns observed in plankton; it is an examination of the possible causes for the residual error. Thus, all of the findings reported here should be evaluated on a species-by-species basis only after inclusion of the major factors into a description of the N-dimensional hyperspace of each species' niche.

A second significant limitation to this approach is the large number of null values present. If only a few lakes had a particular species of phytoplankton, the all values MLR became merely a description of the strongest differences between those lakes and the rest. Although these differences might actually be the cause for the presence of a particular species, the observed patterns of independent parameters often suggested a correlation with something else rather than causality as some of the parameters that would appear early in the MLR had no known physiological value to the species being tested. While this was more of a problem for the summer phytoplankton samples, it also occurred in the sedimentary diatom data. The first solution to this difficulty was to restrict the analyses to only the more common and widely distributed species present, an approach recommended by Gauch (1982) for community analyses.

The second part of the solution to the second limitation due to the large number of zeros was to only look at samples where the species of interest was present. On a number of occasions that inclusion, or exclusion, of null values were found to significantly alter, in both directions, the percentage of explained variance. After several MLR runs the decision was made to look solely at whether or not changes in particular metals changed the relative abundance of a particular species *after* its minimum requirements had been attained. This analytical restriction was made because a number of instances had been observed where another parameter limited the species in question. This second restriction hopefully removed some of the extraneous and confounding factors that influence the final results.

A good example of an extraneous factor affecting results was the diatom *Cyclotella stelligera*. This species was not found in waters with less than 5 mg Cl per liter, but above that threshold chloride appeared to have little significance as its summer abundance in such lakes varied from zero upwards with no detectable pattern in respect to chloride. With chloride in the MLR, nothing else was found to be statistically significant. By restricting subsequent analysis to lakes with $[Cl^-] > 5 \text{ mg Cl}\cdot\text{l}^{-1}$, the summer abundance of this species was determined to significantly correlate with sedimentary organic V. Furthermore, even though Cl concentrations had nothing to do with the summer abundance of another species in this genus, *C. radiosa*), its abundance also correlated

positively to the sedimentary concentration of organic V. The discovery that some members of this genus have a high, and previously unknown, requirement for V, would not have been made without restricting the original analysis to only those cases where the organism was present.

b. The General Validity of Primary Trace Metal Correlations, or How Important is Coincidence?

The problem of coincidental correlations is a very real danger in this research as there were so many independent variables and trace metal ratios tested. By restricting the conclusions to the primary trace metal correlations, and accept a finding only if the same trace metal repeatedly was the primary variable or component of a ratio, the number of random correlations due to the parameter population size was reduced, but probably not eliminated.

A second statistical technique was next applied to reduce this problem. Since a robust regression could also be due to outliers instead of being a coherent response to the parameter in question, after finding the primary variable(s), the data were always plotted in a scatter diagram by lake. A correlation due to a single extreme value, or single lake set, was automatically discounted, while a plot which stayed relatively the same after the removal of one or two outliers, such as *Oocystis pusilla* vs. total available sedimentary copper, had greater credence, although no residual tests were systematically applied to all graphs. (Cook's Distance was initially used several times to discover the common patterns caused by significant biases; the majority of plots were evaluated on the basis of these common responses as the presence of so many (and multiply-caused) non-linear responses discouraged a rigorous examination of each primary correlation.) The relationships possessing such outliers were re-analyzed by stepwise MLR without those data points. Nearly half of all robust primary factor regressions initially observed were due to biasing outliers.

A third method used to reduce coincidental correlations is related to a basic concept of this research, namely a physiological requirement must be known for that metal in the division of the alga or cyanophyte being studied. If there was no known physiological requirement for a particular primary species-independent variable relationship, the finding was discounted. For example, this restriction meant that a positive correlation between the absolute abundance

of an alga and Cu did not prove that particular species of algae had an high Cu requirement. Instead of this hypothesis, the following, physiologically-based, alternative was used. Some algae are known to be more Cu tolerant than are others, or can de-toxify it (Wood and Wang 1983). Under conditions of high concentrations, such species can be freed from competitive pressure by the increased Cu present, hence could grow better under high concentrations than low. These species are not proof for Cu limitation based upon need, but rather demonstrate a competitive advantage due to greater tolerance of this metal.

One quite apparently non-significant trace metal involved in a large number of correlations was cobalt. Except in rare, ultra-low nutrient and dissolved organic material situations, cobalt has never been demonstrated to be limiting. Consequently, except in terms of its relationship to phosphorus or as a denominator for some other trace metal extraction which has been previously suggested to be limiting, any correlation involving cobalt as the primary trace metal tended to be discounted. In other words, organic cobalt was, unless otherwise noted, treated a reference point vis-a-vis other trace metals and not considered to be a limiting factor. The only situations where cobalt appeared to worth further study were the few times that it was the only parameter found to correlate with a particular species and where a relatively large percentage of the data points were fitting into a clear pattern.

Another trace metal which partly fit the Co coincidental pattern was Ni. The only known physiological functions of Ni are in nitrogen metabolism, and the only known use of it in eukaryotic algae is in urease (Oliveira and Antia 1984, 1986; Sunda 1988). Since nitrogen is typically in shorter supply in lakes during the late summer, and urea is produced more during the summer by aquatic animals such as fish and planktonic crustaceans than during the spring, correlations between Ni and common summer or fall diatoms are probably worth further study, thus have been reported. However, the correlation between ExNiFe and the spring-blooming *Asterionella formosa* was obviously a coincidental correlation, so has not been otherwise analyzed.

After restricting the accepted correlations to just the primary one(s), to only those with known physiological roles under the sampled environmental conditions, and to those without apparent outliers, two findings suggested that many of the observed correlations were truly non-coincidental. First, nearly

one-third of all primary correlations had nothing to do with trace metals; i.e., trace metals were not very important to these species. This implied that the correlations involving trace metals were probably relatively robust. Since coincidental correlations are less likely to be robust, this suggested that relatively few coincidental correlations have slipped through these selection procedures.

Second, in the analytical series which included trace metal to major nutrient ratios, there were both several cases where the N:P ratio replaced a trace metal as the primary correlation and, more importantly, ones where the same primary trace metal previously found appeared in a ratio with a major nutrient. The latter situation implied that there might some sort of interaction between this trace metal and the major nutrient, while the former provided a mechanism for eliminating possible spurious correlations such as those with *Pinnularia microstauron* (not that it was necessary for this species given how the data indicated that its Big Lake populations were very high, so that there was an obvious correlative bias towards any outlying parameters found in there.).

None of the methods used can be absolutely guaranteed to have removed all of the coincidental correlations. There are, undoubtedly, a few spurious correlations still in the set of biological results. However, the methods described above should have greatly reduced the prevalence of such, and the observed relative lack of iron results (discussed in more detail below) suggest that Type II statistical errors may have occurred. Given the possibility of Type II errors being present, further attempts to remove potential coincidental correlations do not appear to be warranted.

B. Trace Metal Contrasts

1. Within-Lake Differences

The four lakes which were sampled at multiple locations all possessed clear differences based upon the location of the core. The phenomenon of within-lake differences is a characteristic pattern in sediments (Davis, et al. 1985, Håkanson and Jansson 1983), and can be a significant source of error, so limit the robustness of any conclusions resulting from sediment analyses. The standard methodology for addressing this problem is to sample lake sediments

in the deepest part of the lake (Håkanson and Jansson 1983, Wright 1991) as done here. The specific causes for the particular differences in four study lakes are analyzed on a lake by lake basis in this section, and the limitations and/or overall utility resulting from the observed differences are briefly discussed.

a. Carter Lake

There were three cores taken from two locations in Carter Lake, two in the south basin and one in the, then marshy, neck between the two basins (Figure 5). The south basin had an average dry weight of 80% and a clearly sandy texture while the shallower central station was 70% by dry weight below 10 cm, while in the top 6 cm the dry weight was only 23% of the total. The percent dry weight lost upon ashing was 1.5 and 15.0 %, respectively; i.e. the average amount of organic material was greater in the core from the central station. The top 6 cm of station #2 were distinctly less sandy and more organic than the rest of the sediments.

Fractionated iron and manganese concentrations showed a similar pattern to those of the dry weight and weight lost upon ashing. The HCl extraction averaged 4060 ppm Fe and 34 ppm Mn for the south station, 6070 ppm Fe and 37 ppm Mn at the 20 cm depth of the central station, and 13,400 ppm Fe and 55 ppm Mn in the top 6 cm of the latter core. The pattern for the exchangeable fraction was the same; 30 ppm Fe and 4 ppm Mn, 486 ppm Fe and 27 ppm Mn, and 3360 ppm Fe and 132 ppm Mn, respectively, as it was for iron in the organic fraction, 7.4, 16.3, and 71.1 ppm. Zinc, copper, cobalt, and vanadium in the hot HCl fraction possessed a similar pattern as did Cu, Co, Ni, and V in the exchangeable fraction and V in the organic fraction. In the latter trace metal extractions, the 20 cm depth of the central station had similar concentrations to the south basin samples, while the concentrations found in the top 6 cm were distinctly higher. The residual fraction from the central station had more V than did the south station cores, but no between-station differences were observed for the other six metals in this fraction. Some caution in interpreting the V results should be used however, as the nitrous oxide burner head was changed between the first two cores and the last one, the first core was dried, and none of the values were subjected to an error frequency analysis.

Several interesting conclusions were derived from these results. First, the greater the amount of sand present in a sample, the lower the trace metal concentrations in exchangeable and the oxide fractions there were, but not in the residual or organic fractions, except FeOr and apparently VOr and VRes. This suggested that the sand had relatively consistent and low concentrations of trace metals, and it mainly served to “dilute” oxide, so hence total, concentrations but, due to its coarseness (and probably chemical composition), did not provide a substrate (either in terms of attachment sites or redox condition) for exchangeable trace metals similar to that apparently provided by clays and silts.

Second, the top 6 cm from the central station more closely resemble the sediments from the other three coastal lakes than they do the rest of the Carter Lake samples. The significance of this observation is that it suggests that the biogeochemical processes which form lake sediments on the central Oregon coast are the same throughout the area and that differences between lakes in the area can be mainly attributed to the influences of erosion, i.e. sand being blown or washed into the lakes, and/or the amount of primary production in the watershed and water column.

Third, the small differences observed in the “organic” fraction between the surficial sediments of the central station and the rest of the Carter Lake values points towards a consistent source of organically-bound trace metals, either from autogenic primary production, allogenic inputs of organic materials from the watershed, or diagenic transformations involving sulfur bacteria within the sediments, sulfates in the water column, or sulfides in sedimentary pore water. This implies that the hot peroxide extraction is measuring a process, or processes, with rates of generation specific to the lakes being studied. That is to say, on the basis of just the Carter Lake samples, the “organic” fraction for at least five of the seven trace metals studied is a valid distinguishing lake characteristic, not an artifact of the method of chemical extraction.

b. Woahink Lake

Although the percent dry weight for the 1989 core from the northeast arm of Woahink Lake was only 27% vs. the main station's 21%, the decrease in total trace metal concentrations and trace metals to Al ratios in the top 11 cm

of the 1986 core from this station indicates that over 60% of the material present was sand in this layer, suggesting a percent dry weight closer to 70% than 30%. The 1989 core from this station was taken under conditions of poor visibility due to a light fog, so it may not have been at exactly the same location.

The 1989 Station 2 samples had an average percent loss upon ashing of 12% vs. the main station's 21% and a carbonate or, more likely, water of hydration loss of 2.7% by dry weight vs. 3.2% at the main station.

All trace metals in all extractions at all depths were present in significantly lower concentrations in the sediments of Station 2 with the exception of zinc in the exchangeable fraction. The reductions, using the total available concentrations as an index of the sand dilution effect, were 45.2% for Fe, 26.8% for Mn, 21.4% for Zn, 38.1% for Cu, 39.5% for Co, 30.8% for Ni, and only 18.2% for V. The average reduction in total available concentration was 31.4%, consistent with the reduction in the percent dry weight in the 1989 core.

A large amount of sand was visual in the top 11 cm of station 2. This was probably the sole factor causing the reduction in trace metal concentrations as well as diluted the concentration of organic material characteristic of the deeper depths in the station 2 core and in the main station's core. This dilution was probably due to the same lack of trace metals and organic materials in sand that was noted in Carter Lake sediments.

The specific cause of the increased amount of sand in northeast Woahink is in dispute. Although station 2 is near the entrance of an inflowing stream, so could expected to have a higher concentrations of mineral materials (Wright 1991), the size of this stream is too small to explain the amount of sand present. A forest fire in the northeast part of the lake's drainage basin, hence increased erosion, has been suggested by several people, and support for this idea was found in the form of charcoal particles throughout this section of the core. However, local residents, including a descendent of early pioneers to the area, deny there ever having been a fire in this part of the Woahink watershed since the coming of European-American settlers (Campbell 1994 personal communication). An alternative to the forest fire hypothesis is that the construction of the state park marina on the north peninsula about 1970 involved using a large amount of sand which then spread across the lake bottom. ^{14}C dating of the charcoal at station 2 is probably required to resolve this question.

c. Big Lake

The percent dry weight of the samples taken from the northern end of Big Lake was not directly measured, however similar initial volumes were used for all samples (half of a 1 cm thick slice), and those from the north station were 4 to 6 times as heavy as those from the deep station in the southwest corner of the lake. This suggested that the percent dry weight for the north station was about 50% instead of the 11% found in the deep station. The percent lost upon ashing averaged 31.6% for the deep station of Big Lake, but only 3.3% in the north station core. The percent lost upon ashing tends to be inversely related to the percent dry weight within a lake, and based the amount of dry weight and ash weight from Carter and Woahink, a similar percent dry weight of not quite 50% for the north station was calculated. Both of these dry weight estimates should be only considered to be accurate to the nearest 10%, however.

When compared to core #1, which was treated identically to the core from the north station, there was in the north core less exchangeable Fe (100 vs. 300 ppm), Zn oxides (26 vs. 49 ppm), "organic" and hot HCl-extracted Cu (<1 vs. 14-21 ppm and 15 vs. 50 ppm, respectively), and less V in every fraction, except the residual (4 vs. 34 to 45 ppm VEx, 6 vs. 60 to 122 ppm VOr, 63 vs. 97 to 194 ppm VOx). There was more residual Fe (3.1% vs. 2.2% at 5 cm) and Mn in the HCl fraction (156 vs. 55 ppm), as well as twice as much Ni in the oxide fraction, in the north station core.

Two phenomena are illustrated in the differences between these two stations. The first one is the commonly-observed sorting of particles by size with depth (Davis, et al. 1985, Håkanson and Jansson 1983, Wright 1991) with the finer particles, which have a higher percentage of organic material, being transported into the deeper part of the lake. This phenomenon also explains the lower concentrations of exchangeable Fe, peroxide-extractable Cu, exchangeable V and organic V. Near shore samples, such as the north station, are likely to have a higher concentration of clastic mineral matter (Wright 1991) which explains the larger amount of residual Fe at the shallower station.

The differences between the two stations in the HCl-extracted concentrations for five of the seven trace metals can not, however, be explained by the mechanism of simple physical sorting. There was a consistent pattern of between two and three times as much Zn, Cu, and V in the deep station

sediments as in the north station core while the ratio was reversed for Ni and Mn and absent for both Fe and Co. This may be due to materials formed differently entering the lake from different directions. Bormann and Likens (1979) demonstrated that the type and extent of vegetation interacts with the major ion composition of water draining a watershed. The observed differences between the two Big Lake stations in the trace metals from the "oxide" extraction may be due to this vegetational control mechanism as the Big Lake watershed has a large marsh at the northeast end of the lake, and a burnt over area covered with annuals and early successional vegetation and the barren Hoodoo lava field to the northwest of the lake, while almost all of the forested part of the watershed lies east, southeast, or south of the lake.

d. Crater Lake

The dry weight percentage in the South Basin core was higher than in the Wizard Island shelf core as was the percent lost upon ashing (39.4 vs. 30.4% and 8.7 vs. 6.5%, respectively). Both of these probably only reflect the large depth difference between these two stations (530 m vs. 274 m).

There were no differences observed between the South Basin and Wizard Island shelf cores for any of the Fe, Zn, Co, or Ni extractions, nor for the total available and residual Mn concentrations, although all of the values tended to be slightly higher in the Wizard Island shelf core than in the South Basin. The small differences observed for these extractions and metals were all proportional to either the difference in the amount of water or the amount of organic material present, although the cause for the HCl and residual fractions demonstrating the same trend is not apparent. "Dilution" by unidentified materials with low concentrations of trace metals in the residual and "oxide" fractions is probably the cause. V concentrations in all three available fractions revealed a non-significant increase in the South Basin core over the Wizard Island shelf core. As typically a deeper site will possess finer material (Håkanson and Jansson 1983), it may be that the local geochemical components V occurs in are smaller than average in size.

Residual vanadium, however, is twice as high in the Wizard Island shelf core (72 vs. 36 ppm), and copper shows a similar pattern for all extractions (15.9 vs. 7.4 ppm CuEx, 24.7 vs. 7.3 ppm CuOr, 87 vs. 56 ppm CuOx, and 15.1

vs. 9.4 ppm CuRes). The last observed difference was the distribution within the total available Mn between the two stations. Except for the 2 cm depth of the Wizard Island shelf which was nearly 10 fold higher than the average of the other five values (420 ppm vs. 44.3 ± 12.7 ppm), the peroxide fraction did not differ between the two cores; however, there were strong and consistent differences between the exchangeable and HCl extractions at the two stations. The Mn-oxide fraction was 50% higher in the Wizard Island shelf core (313 vs. 211 ppm), while the exchangeable fraction was nearly three times as large in the South Basin core (433 vs. 156 ppm).

The differences in the Mn concentrations within the available fractions between the two coring sites are probably due to two distinctly different mechanisms. First, the different distribution of Mn between the exchangeable and "oxide" fractions is most likely due to the differences in physical texture between the sediments at the two locations. The exchangeable Mn concentration has been observed to be greater in finer material than in coarser sediments both in other lakes studied here and in comparison between the values from this research and those of Tessier, et al. (1980). The increase in Mn oxides in the Wizard Island shelf core is probably due to *in-situ* oxidation of the exchangeable fraction to Mn oxides within the coarser sediments there.

A second, completely separate, mechanism is required to explain the other unusual feature of the Wizard Island shelf core, the presence of the high concentration of peroxide-extractable Mn at 2 cm. Since the total available concentration was also elevated in this sample as opposed to the other five samples from Crater Lake, an additional local source of Mn appears probable. The increase in Mn concentration in the peroxide fraction may be due a nearby sulfur seep upslope from the coring site with high concentrations of Mn. Dymond and Collier (1990) have observed such seeps in other parts of Crater Lake, so this would be quite likely given the younger age of the Wizard Island cone. Furthermore, Collier, et al. (1990) described increased deep water column concentrations of both Fe and Mn, including near bottom increases in Mn concentrations of one to two orders of magnitude attributed to sulfur springs at the bottom of the lake.

Commercially-valuable copper deposits are known to be associated with recent volcanism and magma chambers (Cox 1979). Since Wizard Island is

more recent than Mt. Mazama, it is logical to assume that there would be an higher concentration of Cu in superficial Wizard Island shelf sediments relative to the rest of Crater Lake. If it is assumed that most of the non-residual V has an external origin, and the magma which produced the Wizard Island cone was either relatively enriched in V compared to that which formed Mt. Mazama earlier, or that V possesses a similar igneous geochemistry to that of Cu, then the increased residual V concentration in the Wizard Island shelf core may be simply due to its more recent volcanic history.

Thus, the two key features which explain the sedimentary differences in Crater Lake are sediment particle size, which is depth related due to within-lake physical sorting, and the role of sulfur springs or seeps in lakes of a volcanic origin or in a geographical area heavily influenced by volcanism.

2. Differences Based Upon Water Chemistry and Productivity

While there were a number of statistically significant contrasts found between the ten original lake classes and either the trace metal concentrations or the 42 trace metal ratios, only two clear patterns were present in this data. First, except for the non-P-limited, oligotrophic lakes, trophic status by itself was not an important factor. Lake productivity contributed to class separations, but there was only one situation where it distinctly differentiated between two classes with the same conservative ion chemistry, exchangeable Co in the high conductivity lakes. Apparently, changes in sedimentary trace metal concentrations are not typically associated with changes in productivity. Second, most of the observed differences were between the hard water, high alkalinity lakes and the other four groups of the redefined classes, with the high P, oligotrophic lakes the next most distinctive.

The amount of divalent ions, i.e., water hardness, was considered to be the most significant conservative water chemistry parameter of the three used in the original system of classification (hardness, alkalinity, and conductivity). First, the hard water, high alkalinity lakes were the most often distinguished lakes in the three data sets of trace metal-lake class comparisons considered in this analysis (35 of 53 significant differences in the redefined lake classification), and second, neither the high conductivity nor the high alkalinity lakes were typically associated with the hard water lakes when these lakes had

significant contrasts to other lakes. Indeed, 12 of the 35 significant contrasts that the hard water lakes had were with these two groups, 22.6% of the total found. The lack of importance of the alkalinity concentration in differentiating trace metal concentrations also allowed the successful subsequent merger of the two high P, oligotrophic lake classes as they were otherwise chemically identical.

The relative insignificance of alkalinity in these contrasts further supports the notion that trophic status is not important as alkalinity appears to be weakly associated with lake productivity (Wetzel 1975).

The relative strength of water hardness vs. alkalinity or conductivity for correlations with sedimentary trace metal concentrations also makes sense in terms of trace metal biogeochemical cycling. Hardness is a measure of the amount of divalent cations present in the water column, and the concentration of divalent cations is related to the amount of easily eroded minerals in a lake's watershed. Since limestone is not a common source rock in Oregon, unlike in the American Midwest (Alt and Hyndman 1978, Tarbuck and Lutgens 1984), most of the rocks being eroded in Oregon also have high concentrations of trace metals, primarily iron. Thus, if there has been quite a bit of erosion in the watershed, there should be large concentrations of divalent cations transported to the lake. As a consequence, both hardness and the amounts of sedimentary trace metals will reflect their watershed geochemistry and "erodability" with the soluble cations remaining in the water column while the relatively insoluble divalent cations, i.e., six of the eight trace metals studied, precipitate out. If there is a large supply of one group, the solubles as measured by water hardness, present, then it is reasonable to assume that one or more trace metals is probably also being added to the lake from its watershed in increased quantities, hence the observed relationship.

The unique nature of non-P-limited oligotrophic lakes may just be related to their extreme oligotrophy; even Lava, a more-or-less mesotrophic lake, ought to be hypereutrophic given the amount of P present, thus it too can be said to be "relatively ultraoligotrophic". However, Big Lake, which is a true ultraoligotrophic lake, is P-limited, so this explanation is rather weak, and the existence of other ultraoligotrophic Oregon lakes limited by P further argues against accepting such an explanation. A more likely alternative is that

nitrogen fixation in these lakes is limited by trace metals so there is insufficient nitrogen for adequate phytoplankton growth, hence they have not become P-limited (Rueter and Petersen 1987). However, the limiting trace metal these lakes is not necessarily Fe or Mo; as discussed below, Ni may limit cyanophytes in some situations, and insufficient Zn may restrict diatoms in some oligotrophic lakes before either nitrogen or phosphorus become limiting.

While these comments are vast oversimplifications of the significant contrasts described previously, these general patterns are the only consistent ones which clearly emerged.

3. Differences by Ecoregion

Although the diversity of significant findings and their relative lack of distinctive patterns also make general conclusions characterizing lake trace metal chemistry difficult to reach based upon the effects of ecoregions, one observation clearly stands out about this effort. The ecoregion approach explains more about the distribution of sedimentary trace metals than does the alternative. There are two basic reasons for stating that ecoregions explain more about the distribution of sedimentary trace metals than does classifying the lakes by their water chemistry and productivity. First, on a quantitative basis, more significant contrasts are found per ecoregion (13) than are present by lake class (9.9, or 10.6 for the redefined classes). Furthermore, the majority of the differences observed in the water chemistry classes are due to one factor, the concentration of divalent ions, or hardness. If that factor is removed from consideration, the remaining 16 soft water lakes have few significant differences in water chemistry by which to sort them (for the redefined lake classes, the number of contrasts per class is only 4.5, a threefold reduction from the number of contrasts per ecoregion).

Second, using an ecoregion approach allows qualitative predictions to be developed. With only water chemistry classes, the differences within the 16 soft water lakes of this study are obscured; by using the ecoregion concept, several significant differences appeared between the Coastal lakes and the Coast Range lakes and more appeared between both and the Cascade lakes. Moreover, when just the three ecoregions where hard water lakes are present are compared, eight significant trace metal contrasts were found from among

the 21 extractions. (Details of some of these differences are described later in this section.) But, more importantly, physical causes and geological mechanisms explaining these differences can be identified and broader hypotheses, than available using water chemistry only and extendible to other lakes, can be developed. That is to say, ecoregions are a concept which allows the development of predictive models with respect to trace metal distribution. Part of the reason that ecoregions explain more of the between-lake variability than does water chemistry is that ecoregions are explicitly based in part upon soil composition. The causes of soil formation within an ecoregion are frequently also the same mechanisms which formed the majority of lakes there. Furthermore, the soil is typically the main source material for the trace metals found within the lakes.

The most distinctive lake-specific and ecoregion differences can be observed by examining the contrasts found within the hard water and soft water groups. In most of these situations, the causal mechanism appears to be related to the geology of the lake, including its origin and watershed.

Fifteen of the 16 soft water lakes studied are found in the Coastal, Coast Range, Cascades, and Blue Mountain ecoregions. While the Coastal, Coast Range, and Willamette Valley ecoregions all have a Maritime climate, their soils are different and their lakes have a different origin. The differences between the Coastal and Coast Range subcoregions, except the amounts of conductivity present and sand as a soil source, are more-or-less a matter of degree. Coast Range lakes differed significantly from Coastal lakes by having more organic Co, though the amounts of organic Ni and total available Zn were more similar between the Cascades and Coastal lakes than either was to these lakes. The relative absence of significant trace metal differences between lakes of the Coast Range and lakes from the Coast proper supports the idea that they are not very distinct from each other, despite having a clear contrast in their water chemistry. This lack of contrast is implied in Omernik and Gallant (1986) and has been explicitly suggested by Omernik (1992 personal communication). By contrast, significant differences were observed between the Cascades vs. the Coastal and Coast Range lakes for exchangeable Cu (Cascades were higher), exchangeable Fe (Cascades lower), total available Fe (Coast Range greater than Cascades), exchangeable Mn

(Cascades lower), total available Mn (Cascades lower), all forms of V (Cascades higher), and exchangeable Zn (Cascades higher). On the other hand, the two soft water Blue Mountain lakes are very average in terms of their trace metal concentrations. They have only two significant differences, one with each of the other two major ecoregions with soft water lakes; they have significantly lower CuEx concentrations than the Cascades and are lower in organic V than the Coastal lakes.

Climate does not appear to be the primary cause for ecoregion differences. In Maritime western Oregon, everything except climate is different between the Coast ecoregion and the Willamette Valley ecoregion. In the Valley, the water chemistry is hard, most lakes originated as abandoned river channels such as backwaters or oxbows, and the soils are lacustrine deposits from eastern Washington Columbia River basalts; i.e., twice worked over volcanic rock, but still relatively rich in dissolvable cations. Differences within the Montane ecoregions also appear to be of geological origin. The Cascades and Eastern Transition ecoregions are still active volcanic areas, while both the Blue Mountains and the Siskiyou are from the Triassic (Alt and Hyndman 1978). In addition to the difference between Cascade and Blue Mountain soft water lakes mentioned before, there are two significant differences between the hard water Siskiyou and Newberry lakes of the Eastern Transition, total available Cu and Ni concentrations.

The Eastern Transition ecoregion is a transition zone between the Cascade and the High Desert ecoregions both in terms of the evaporation: precipitation ratios and vegetation, and in terms of recentness of volcanism, with an east-west gradient running from dry and dead to wet and active. Most of the lakes of this ecoregion are located in the newer part of it. Their volcanic origin, along with most of the Cascade lakes studied leads to several interesting sedimentary trace metal characteristics which are explainable on the basis of their origin, but not on the basis of their water chemistry. East and Paulina in Newberry and Crater in Mazama are recently formed lakes within recently active calderas. The Newberry lakes are hard water while Crater has soft water, yet all three caldera lakes possess a distinctive sedimentary chemistry and appear to be more similar to each other than to other lakes in these two ecoregions. Their hypolimnetic water chemistry also resembles that of

Myvatn, a lake with numerous hot springs in Iceland (Dickman, et al. 1993, Jónasson 1993). This similarity appears to be due to the presence of hot springs or of “warm” seeps in the bottom of these lakes. All three lakes have sedimentary Mn concentrations in the peroxide extraction near, or above, 100 ppm, much higher than the other study lakes with one exception. These values are not related to the amount of sedimentary organic material or to the amount of phytoplankton in the water column, so non-easily oxidizable Mn sulfides may be the sedimentary source material causing these elevated values. The Mn sulfides appear to come from sulfur springs of very recent volcanic origin. Such hot springs are known to exist in East on the southeast side of the lake and in Paulina (Johnson, et al. 1985), while Dymond and Collier (1990) found warm seeps in the South Basin of Crater Lake and Collier, et al. (1990) recorded large increases in hypolimnetic dissolved Mn in Crater Lake, much as has been observed over geothermal vents along Gorda Ridge off Oregon (Collier and McMurray 1988 personal communications). Peroxide-extracted Fe is also very high (>1000 ppm) in East while Paulina have very high concentrations of FeOx and Crater has higher concentrations of this extraction than any other lake in these two ecoregions except Paulina as well as high Fe concentrations in the hypolimnion (Collier, et al. 1990). “Organic” Ni also has a similar pattern with Paulina possessing one of the two highest concentrations observed during this study.

Only one other lake in this study possessed a similar sedimentary trace metal geochemistry to these three lakes, Todd. Peroxide Mn was above 100 ppm, more than in Crater, and peroxide Fe was also above 1000 ppm. Furthermore, Todd was the only other lake with the very high concentrations of “organic” Ni. A possible cause for these high Todd Lake values may be the suspected recent volcanic activity by South Sister (discussed further in section IV.D.1).

The sediments from all of the coastal lakes in this study except in the south basin of Carter, had exchangeable Fe concentrations in excess of 2000 ppm, regardless of trophic status or water chemistry. With two exceptions, Oswego and Todd, no other lake sampled had FeEx concentrations greater than 1000 ppm. All of the analyzed coastal lakes are near Florence where ground water concentrations of dissolved Fe are quite high (Cooper Consultants 1985; Sweet

1990). The coastal lakes, again excepting Carter, are all apparently P-limited, while Carter is oligotrophic with $40 \mu\text{g tdP}\cdot\text{l}^{-1}$, i.e., clearly not P-limited. The initial response to this correlation between low exchangeable Fe and the lack of P-limitation was to hypothesize that there might be a causal relationship; this was subsequently disproven as summarized below.

Carter is not the only oligotrophic-high P lake in the Florence area; Clear, Lane Co., Munsel (both sampled) and Collard Lakes also fit the same trophic status and water chemistry profile, either completely (Clear), or partially (Munsel and Collard). Cores from Clear Lake also quickly developed surface deposition of iron oxides on the core liners due to the diffusion of atmospheric oxygen through the Lexan and oxidation of the dissolved iron in the sediments. Since these deposits appeared on the core liners of all lakes possessing exchangeable Fe concentrations over 1000 ppm, it is highly probable that Clear Lake, Lane Co., also has exchangeable iron concentrations above 1000 ppm, a hypothesis supported by observations from other studies (Cooper Consultants 1985, Sweet 1990). Therefore, the oligotrophic-high P status of Carter Lake is probably not related to its low mean exchangeable iron concentration.

The low exchangeable sedimentary iron concentration in Carter Lake appears to be due to its shallow depth (maximum = 3.7 m) as the next most shallow coastal lake sampled (Mercer) was over 11.5 m. The ground water flowing into the other lakes is believed to originate from deep aquifers which probably are de-oxygenated and in contact with high iron-containing soils and/or rocks, hence, develop the high Fe concentrations observed in study lake sediments (Cooper Consultants 1985, Sweet 1990). The depth difference between Carter and the other coastal lakes means that all of the water flowing into Carter was probably superficial recent precipitation traveling through the local quartz sand dunes instead of being ground water. Further support of this idea was found in the 12 October 1977 vertical profile made by the U.S.G.S. (1979); both dissolved oxygen and temperature were homogeneous with depth in Carter Lake while Eel and Clear Lakes, Douglas Co., sampled later the same month, still had thermoclines (beginning at 10 and 16 m deep, respectively).

The specific significant differences among the hard water lakes of the three ecoregions where they occur include between Squaw Lake and the Newberry lakes for total available Cu, between the Eastern Transition lakes and

Willamette Valley lakes for organic Fe, Mn, and V, between Squaw Lake and the Willamette Valley lakes with regard to exchangeable Ni, and between the Eastern Transition lakes and the hard water lakes of both western Oregon ecoregions for organic Ni and total available Zn, while Squaw Lake had more total available Ni than the other four hard water lakes. Clearly hardness does not explain all variability between the different lakes for either category.

The sedimentary trace metal chemistry of Squaw Lake supports the idea that the Siskiyou have a unique geological origin. The high sedimentary Ni concentrations present appear to be due to the Ni-bearing serpentinite deposits located throughout these mountains (Alt and Hyndman 1978), a unique feature not only to Oregon but apparently to most of North America as the only U.S. nickel mine is located in Riddle at the northern end of the Siskiyou (Alt and Hyndman 1978) while the big Ni mine in Sudbury, Ontario, is apparently the result of a meteor (Nriagu, et al. 1982). The Zn in Squaw Lake appear to be due to local deposits of galena, or zinc sulfide. There are, or were, numerous metal ore deposits in the Siskiyou, mostly of gold, chromium, copper and platinum (Alt and Hyndman 1978). Since Cu deposits in the Pacific Northwest are frequently associated with zinc (Highsmith and Kimerling 1979), zinc deposits, hence high sedimentary Zn in lakes, may be typical of the Siskiyou as well.

In summary this evidence indicates that, while the concentration of divalent ions and climate are important factors influencing the concentrations of trace metals in lake sediments, aquatic ecoregion differences are more than just water chemistry and weather differences; the geology of the lake is an important factor. Furthermore, using the ecoregion concept explains more of the variability in sedimentary trace metal concentrations than does hardness alone, the only significant water chemistry parameter found in this research.

4. Anthropogenic Impacts

Recent increases in trace metal concentrations in superficial lake sediments due to human activities have been extensively documented (Carignan and Nriagu 1985, Carignan and Tessier 1985, Charles and Norton 1986, Charles, et al. 1987, Crecelius 1975, Davis, et al. 1983, Davison, et al. 1985, Dunnette 1983, Engstrom and Wright 1984, Förstner and Wittman 1979,

Galloway and Likens 1979, Hamilton-Taylor and Willis 1990, Hendriksen and Wright 1978, Johnson 1987, et al. 1986, Kerfoot, et al. 1994, Lee 1983, Moore, et al. 1988, Norton, et al. 1978, 1992, Nriagu 1979, 1983, et al. 1979, 1982, Nriagu and Wong 1983, Ochsenbein, et al. 1983, Rabe and Bauer 1977, Rippey, et al. 1982, Sigg 1985, et al. 1987, Snodgrass 1980, White and Driscoll 1987a, White and Gubala 1990). Three mechanisms appear to cause these increases; first, atmospheric deposition, with (Birks, et al. 1990, Cowling 1982, Charles and Norton 1986, Dixit, et al. 1993, Galloway and Likens 1979, Havas, et al. 1984, Hendriksen and Wright 1978), or without, acid precipitation (Cook, et al. 1990, Crecelius 1975, Engstrom and Wright 1974, Hamilton-Taylor and Willis 1990, Johnson 1987, Johnson, et al. 1986, Nriagu, et al. 1979, 1982, Vesel'ny, et al. 1993), or before it occurred (Charles, et al. 1990); second, direct discharge of industrial and other urban sewage into a water body (Dunnette 1983, Förstner and Wittman 1979) or the discharge of mining wastes (Davison, et al. 1985, Kerfoot, et al. 1994, Rabe and Bauer 1977); and third, increased erosion due to changes in land use practices, particularly those associated with deforestation (Bradbury 1986, Charles, et al. 1987, Hickman, et al. 1990, Kingston, et al. 1990).

Acid precipitation is not currently thought to occur in Oregon (El-Ashry, et al. 1985, Laird, et al. 1986) and, outside of the Portland metropolitan area, heavy metal pollution due to direct industrial and domestic discharges is both localized and limited to a few metals, primarily zinc (Dunnette 1983). In the Portland area due to both industrial and urban discharges into the lower Willamette and Columbia Rivers, high sedimentary concentrations of Zn, Cr, Pb, Cu, and Ni are found (Dunnette 1983). While mining wastes can be a serious problem, mining is not a large source of water pollution in this state, barring the small Ni mine at Riddle and gold mining in the Siskiyou and Blues. Indeed, mining as a source of trace metals in Oregon waters was not even included by Dunnette (1983). This leaves only non-acidic atmospheric pollution, known to occur here (Dunnette 1983), and increased erosion due to deforestation as major sources of increased sedimentary trace metal concentrations in Oregon lakes and rivers with one, locally-significant, addition, Lake Oswego.

Copper, zinc, nickel, and vanadium, along with lead, cadmium, mercury, arsenic, and sometimes selenium, are used as indicators of anthropogenic inputs;

iron and manganese are also usually measured in such studies as well along with aluminum and occasionally titanium, (Charles and Norton 1986, Charles, et al. 1987, 1990, Johnson 1987, et al. 1986, Vesel'y, et al. 1993). The four commonly used indicators are Pb, Cu, Zn, and V (Birks, et al. 1990, Charles, et al. 1990, Kingston, et al. 1990, Norton, et al. 1990, Vesel'y, et al. 1993). Manganese remobilizes in acidic lake sediments (Charles, et al. 1990), acting as a conservative dissolved cation in the water column of those lakes (White and Driscoll 1987b), so sedimentary Mn/Al and Mn/Ti ratios are considered to be better indicators of environmental change (Charles, et al. 1987). Iron is not useful as all studied lakes with an oxygenated hypolimnion have a sharp increase in total Fe just below the sediment-water interface (Charles and Norton 1986, Cook, et al. 1990, Vesel'y, et al. 1993). The vertical distribution of cobalt has not been studied as a possible indicator of anthropogenic change.

In Oregon atmospheric zinc contamination due to coal combustion, direct discharge of Zn from pulp mills, and atmospheric Pb contamination from automobile exhaust are considered to be the major sources of pollution outside of the Portland metropolitan area (Dunnette 1983). Lead was not investigated in this research and no evidence for Zn contamination was found in the sediments of the 21 lakes studied by sequential fractionation. However, this is not to say that Zn contamination does not exist in these lakes, only that it was not directly observed (however see the discussion of the *Melosira ambigua* results below). The vertical resolution of this study was inadequate to detect changes in concentration due to pollution during the AAS analysis with one exception, Cu, while the more finely physically segmented INAA did not measure Cu, Zn, Ni, or Pb. This left only vertical profiles of total V and As by INAA from Woahink, Eel, and Munsel Lakes to analyze for possible signs of pollution.

a. Copper

The low concentrations of sedimentary copper observed in all of the lakes in this study, excepting Lake Oswego and the previously-discussed Wizard Island core from Crater Lake, are also typical of most non-polluted European lakes, especially Windermere (Hamilton-Taylor and Willis 1990, Reynolds and Hamilton-Taylor 1992, Sigg, et al. 1987) and of non-urban North American lakes before industrialization and its accompanying air pollution problems

(Cook, et al. 1990). This appears to be a phenomenon related to the overall failure of dissolved Cu to be incorporated into the sediments via most chemical precipitation reactions, largely due to the fact that it forms complexes with dissolved organic materials (McKnight 1981, Sigg 1985).

The exception of Lake Oswego is mainly due to the enormous additions of copper sulfate as an algicide which have exceeded the solubility products for this metal as well as the capacity of the dissolved organic materials present in this lake. A comparison between Clear and Oswego Lakes demonstrates this as these lakes possess a similar water chemistry and trophic status thus a similar distribution of copper within the sediments should be expected. For both lakes, the exchangeable Cu concentration averages 1.4 ppm, and the residual Cu concentration at 5 cm is between 4.5 and 7.5 ppm. The peroxide extraction increases in concentration between Clear Lake and Lake Oswego from 4.4 to nearly 70 ppm with a minimum in Lake Oswego of over 40 ppm, while the average of the HCl extractions increases from 33 ppm in Clear Lake to 230 ppm in Lake Oswego. It appears that all of the added Cu in Lake Oswego is present in the sediments either in the HCl or peroxide extractions.

The added copper may be transported to the sediments in one of four possible ways, first, through biological uptake by the algae, followed by their deaths and sinking to the bottom (McKnight 1981), as desired by the Oswego Lake Owners Association; second, through the formation of a copper carbonate precipitate (Sanchez and Lee 1978); third, formation of copper hydroxide or copper phosphate precipitates (Benjamin and Honeyman 1992, Sanchez and Lee 1978); and fourth, by precipitation of copper sulfide in the anoxic hypolimnion (Sanchez and Lee 1978). Although mining occurred in the Lake Oswego drainage basin, it was for Fe, not Cu, so the physical transport route by fine mining tailings as described by Kerfoot, et al. (1994) is highly unlikely to have occurred in Lake Oswego. Since the total amount of sedimentary carbonate in Lake Oswego can be no more than 3.6% by dry weight, copper carbonate precipitation is also unlikely to be a major route. Because three-quarters of the increase in sedimentary Cu between Clear and Oswego is found in the HCl extraction and redox changes do not liberate this metal once it is incorporated in the sediments (Balistrieri, et al. 1992), the primary route(s) of Cu to the sediments of

this lake appears to be as copper hydroxide, or as copper phosphate, or due to both.

Some of the increase in the peroxide extraction is probably due to precipitation as CuS when the added copper sulfate is dispersed below the thermocline into the typically anoxic hypolimnion of this lake. How much of the peroxide extraction is sulfide and how much is organic material is not known however. While the sediments were dark and had a slight "sewer" odor to them; they were not black, which they would be if FeS was present in high concentrations, and they did not smell of hydrogen sulfide. These observations suggest that more of the peroxide fraction was organic in origin than was not. In conclusion, based upon these observations, probably no more than between 12 and 20% of the added Cu to Lake Oswego is sequestered in the sediments as organic copper.

It seems likely that most the remaining Cu present in the Lake Oswego water column a few days after the copper sulfate additions is in dissolved organic complexes (McKnight 1981, Hamilton-Taylor and Willis 1990, Reynolds and Hamilton-Taylor 1992, Sigg 1985, Sigg, et al. 1987, Wagemann and Barica 1979, Wilson 1978, Xue and Sigg 1993). These complexes are relatively harmless to phytoplankton (McKnight 1981, Paerl 1988, Wurtsbaugh and Horne 1983).

The results found here and the literature cited suggests that most of the added copper sulfate is ineffective for the long term control of algae in Lake Oswego. First, a majority of it is quickly precipitated out of the epilimnion in a form which does not affect the phytoplankton and what remains is apparently transformed into non-toxic complexes with dissolved organic material. Second, Oswego was one of only two lakes in this study where Cu-tolerant species of algae were observed. Since Oswego is considered to be hypereutrophic (Johnson, et al. 1985) with algae problems this suggests that the phytoplankton are being selected for Cu tolerance by these additions rather than actually being controlled.

Since the copper sulfate appears to be selecting for different species of phytoplankton rather than controlling overall primary production, possibly the lake owners association should consider another method to improve the water quality. Phosphorus control seems to be a better way than the present system

as Lake Oswego is hypereutrophic due to the high concentrations present (Johnson, et al. 1985). The largest single source is probably the Tualatin River (Johnson, et al. 1985; Vaga 1992 personal communication). This hypothesis is supported by the following observation. When the dam turbine was shut down for repairs a few summers ago, the deepest Secchi Disk measurements ever recorded in Lake Oswego were observed by both Geiger and Sweet (personal communications). Since the Tualatin receives much of its phosphorus through non-point and natural sources (Vaga personal communications), it is not likely to be successfully and/or cheaply controlled. Consequently, probably the fastest way to improve water quality would be to permanently shut down the dam turbine.

A second major P source is lawn fertilizer (Johnson, et al. 1985, Geiger personal communication). If the city council banned the sale of P-containing lawn fertilizer as an additional measure to control direct P additions to Lake Oswego, it might also improve this situation.

b. Vanadium

Total vanadium profiles, either by itself, or in a ratio with aluminum, showed no evidence for increased deposition of this metal in either Eel or Munsel Lakes (Figures 11 and 13). However, an increase was observed both in the total vanadium concentration and in the ratio of total V to total Al in the core from the mid-lake station of Woahink (Figures 9 and 15). The increase in total V began at 10 cm and the increase in the total V:Al ratio started at 4 cm. The latter increase was apparently due to atmospheric inputs from oil combustion while the former marker appears to have been caused by increased erosion as Al concentrations apparently increased at the same time. These findings are discussed further in Section IV.D.2.

c. Arsenic

There was an increase above 10 cm in the total arsenic concentrations in sediments from Eel, the mid-lake station of Woahink, and one core from Munsel; however when the As:Al ratios were plotted, the only significant increase found was in one Munsel core (Figures 100 and 101). Atmospheric As covaries with Zn (Johnson 1987), mostly coming from smelters and coal ash (Charles

Figure 100. Vertical profile of the As:Al ratio in Munsel Lake sediments.

Figure 101. Vertical profile of the As:Al ratio in Woahink and Eel Lake sediments.

and Norton 1986). The Munsel Lake As profile suggests, but does not prove, that there may be increased local Zn deposition found in the superficial sediments of some Oregon lakes. As zinc pollution from both general atmospheric inputs and direct discharges is believed to be widespread across Oregon (Dunnette 1983), further coring efforts to analyze for vertical changes in the concentrations of sedimentary Zn are recommended on the basis of Dunnette's assessment and the Munsel sedimentary As finding.

C. Phytoplankton and Sedimentary Diatom Comparisons

1. Based upon Water Chemistry, Productivity, and Ecoregion

a. Water Chemistry and Biological Productivity

There were surprisingly few correlations found between phytoplankton and sedimentary diatoms when regressed against either water chemistry or biological productivity. Only five water chemistry parameters, calcium, chloride, alkalinity, conductivity, and percentage of sedimentary carbonate, had any strong correlations, and just two indices of biological productivity, percent organic material in the sediments and the mean trophic status index, were primary correlating factors with individual species of phytoplankton and/or sedimentary diatom remains. The overall pattern found through the cluster analyses supported this paucity of definite correlations with individual environmental parameters as the cluster analyses showed more similarity with ecoregions instead with any one or two individual physical or chemical parameters. However, this lack of positive results should not be viewed as proof that water chemistry or biological productivity indices do not affect most of the species analyzed, only that these parameters are not the most important ones for determining the distribution and abundance of individual species.

The two most interesting biological findings to come out of this part of the analysis, other than the verification by cluster analysis of the ecoregion concept, were the lack of correlations with water hardness, unlike the situation for the trace metals themselves, and the observation that species of summer phytoplankton which correlated with biological productivity tended to have weak, or no, correlations with trace metal concentrations, and vice versa. The chrysophyten flagellate, *Kephyrion spiralis*, was the only species which strongly correlated with the predominant cation involved in water hardness,

calcium. Alkalinity and sedimentary carbonate, two direct measures of water column alkalinity and an indirect measure of hardness, added only three more taxa to this list, for a total of four, or less than 10% of the total number analyzed. Two of these three taxa possessed quite strong correlations however, so these were not coincidental correlations, suggesting that this scarcity is a “real world” phenomenon. (The two strong relationships were *Nitzschia frustulum* with alkalinity and the “small *Stephanodiscus*” taxon with sedimentary carbonate.)

The four species which increased in abundance above a minimum threshold mean trophic status were either large diatoms or cryptophytes. The lack of strong correlations with trace metals combined with the apparent relative ease of culturing such organisms suggested a mechanism to explain the absence of positive findings when trace metals are added in enrichment experiments. If only the easily cultured species, characteristic of more eutrophic conditions, are studied or respond more to environmental changes such as fertilization studies, yet these species are among the least responsive to trace metals, then the trace metal addition experiments which focus upon changes in productivity will miss most of the effects of the addition and only observe the weaker, or less distinct, responses more typical of these relatively insensitive species.

A second observation based upon these findings is that there is a clear difference between large marine and fresh water diatoms in terms of sensitivity to trace metals. More accurately, large marine diatoms in blue water oceanic environments have been demonstrated to require iron (Chisholm and Morel 1991, Hutchins, et al. 1993, Kerr 1994); this research did not document a large iron requirement for similarly sized diatoms in oligotrophic fresh waters.

There were several species distribution patterns noted using the percent sedimentary organic material as an indicator of lake productivity. The first feature observed was that, unlike with the mean trophic status index, weak trace metal correlations were consistently found with each species; however, the key word in the preceding phase was “weak.” The second characteristic was that different species possessed different optimal levels of lake productivity. For example, *Achnanthes minutissima* became less relatively common in the sediments with increasing percent organic material, while *Tabellaria*

fenestrata became more common. There were also two cases of within-genus replacement with changing concentrations of percent sedimentary organic material, *Amphora* and the "small *Stephanodiscus* taxon," discussed in more detail in section IV.C.2.g. None of these examples, except with regards to which particular species responded to these changes, were scientifically interesting or important however, because such responses and replacements were expected ecological patterns (Gauch 1982, Whittaker 1956, 1962, 1967). The interesting scientific peculiarity of this situation was the relative scarcity of such relationships as primary correlations.

It appears, based upon the low number of primary factor results from both the mean trophic status index and the percent sedimentary organic material, that lake productivity is not a very good predictor of species composition. This relative insignificance may simply be due to inclusion of more parameters in the models, hence a higher likelihood of random matches having higher significance than productivity indices. However this does not seem likely because there was a pattern of higher correlations of both trace metals and species composition with ecoregions as well as physiologically based matches between individual species and trace metals. This pattern suggests species-specific causality and responses rather than coincidence.

The results found in this research support, but do not prove, two rather abstract but interesting hypotheses previously discussed in the literature. The observation that trace metal ratios relate to species richness, but neither correlate strongly to lake productivity conforms to Tilman's (1982) second evolutionary prediction. Some of the results also appear to support the concept of simultaneous resource limitation by multiple nutrients, similar to what Brand, et al. (1983) and Sunda (1988) found. Neither proof, though interesting, is particularly strong however.

b. The Centrality of Ecoregions

Several different lines of evidence strongly suggest, but do not prove, that Omernik and Gallant's (1986) ecoregion concept is valid for lake phytoplankton and lacustrine sedimentary diatoms. Furthermore, the nature of this evidence raises the possibility that this relationship is at least partially correlated with, if not caused by, variations in trace metal concentrations.

Although the two cluster analyses do not possess simple and neat explanations for their distribution patterns, nevertheless, the results of these analyses are very similar, thus suggest that there is a strong underlying reality shared by them. This commonalty exists despite that these analyses cover two different groups of organisms which only partly overlap, and that the original identifications were made by several different people. The similarities are as follows: The primary split in both cases was the six lakes of the Coastal ecoregion from the others. Lower level clusters in both analyses included the Newberry Caldera lakes, Walton, Morgan and Lava together, Clear with Oswego, Lake of the Woods with Todd, and Triangle with Loon. Except for the inclusion of Lava with the Blue Mountain lakes, all of these clusters are based upon ecoregions; Lava's inclusion with Walton and Morgan may be due to its mesotrophic status and that it has a Montane climate and soft water. The next closest lake to the Newberry ones was South Twin for the summer phytoplankton, and Crater for the sedimentary diatoms, or respectively within the same ecoregion, and having a common geological origin, so probably similar epibenthic substrates.

In the summer phytoplankton, unsurprisingly Blue and Crater form a cluster, and the eutrophic Suttle Lake eventually joins the other eutrophic and mesotrophic Montane lakes, though the sedimentary diatoms of these two lakes form a clear pair. There are several possible causes for this difference; the most likely one is that sedimentary diatoms record both epibenthic species and non-summer forms, both of which could be more similar than the summer assemblages. The two lakes are, after all, sequentially joined in the same watershed less than a kilometer apart. Furthermore, Blue Lake has a deep chlorophyll maximum, which has not been sampled very often, and some nitrogen fixation (Mulvey 1986), and the Suttle Lake Forest Service campgrounds, the apparent source of its extra nitrogen, are not used year round.

Squaw joined the hard water eutrophic Willamette Valley lakes in the sedimentary diatom cluster analysis while its summer phytoplankton was part of the mesotrophic to eutrophic Montane cluster. This suggested an intermediate position for this lake between these two groups. Also the summer phytoplankton of Big Lake combined with those of the oligotrophic, high P Cascade lakes

to form the next larger cluster there, apparently due to its ultra-oligotrophic mean TSI.

The largest mismatch in the summer phytoplankton analysis was the inclusion of the Lake of the Woods-Todd pair with the Coastal lakes, while the addition of Big Lake to the Blue Mountains-Lava cluster was the biggest mismatch for the sedimentary diatoms.

In summary, the Coastal lakes are clearly distinct as are the Willamette Valley lakes, and the two Coast Range lakes form a subgroup of the Coastal ecoregion while the Montane lakes have more heterogeneous clusters; although the Blue Mountain lakes, the Newberry Caldera lakes, and Lake of the Woods plus Todd form clear subclusters.

Part of the reason that the Coastal lakes are as clearly separated from the others is apparently their water chemistry. All five species observed to correlate with conductivity and chloride increase in abundance with increasing concentration or required a minimum salinity before being found. These five species primarily, or solely, occur in the Coastal lakes, and this subassemblage, though low in species richness, is apparently an important differentiating component as at least one of the "chloride-limited" species, *Cyclotella stelligera*, is abundant in these lakes and nowhere else. Thus, these chemical parameters may partly cause the biological uniqueness of this ecoregion.

Despite the relative importance of the water chemistry parameter of hardness, it is not the most important factor controlling phytoplankton and sedimentary diatom distribution or the cluster analyses would have shown more combination by the five hard water lakes, the Newberry caldera lakes, the Willamette Valley lakes, and Squaw. Except that they were not Coastal lakes, the summer phytoplankton of these five lakes were completely separate. Squaw and the Willamette Valley lakes did form a second tier cluster for the sedimentary diatoms; however, these three lacked any association with the Newberry lakes, except again not being Coastal lakes. Conversely, trophic status seemed to play a larger role in the formation of clusters, especially for the summer phytoplankton after the primary split between the Coastal and non-Coastal lakes.

These patterns support the notion that ecoregions are at least partially valid for phytoplankton and sedimentary diatom remains. There are clear

inadequacies to this model, or else there would have been a perfect or near-perfect fit, but the overall pattern of the cluster analyses suggest that ecoregions have a “real world” basis, and that applying this concept to phytoplankton and lacustrine epibenthic diatoms, as Whittier, et al. (1988) did to Oregon stream chemistry, periphyton and invertebrates, is useful and describes an actual phenomenon.

Separately discovered from the cluster analyses of phytoplankton and sedimentary diatoms is the fact that more of the variations in trace metal concentrations can be explained by ecoregions than by water chemistry and/or lake productivity. Also, as discussed in Section IV.B.2, trace metals do not appear to affect aquatic productivity except under extreme circumstances while, as discussed in the following section, variation in the concentrations of individual trace metals can be shown to cause species-specific responses.

Since variations in trace metal concentrations seldom impact overall lake productivity, yet may alter phytoplankton species composition, and since both the phytoplankton/sedimentary diatoms and trace metals appear to correlate better with ecoregions than with the alternative water chemistry-lake productivity model, this leads to the following hypothesis: Regional trace metal variability in the underlying watershed geology is responsible for a significant part of the mechanism(s) causing ecoregions.

Omernik and Gallant (1986) clearly state that both climate and soils contribute to produce these associations. Different trace metal ratios can be derived from selective erosion of bedrock and soil components, while this research indicates that changes in trace metal ratios correlate with changes in species composition and might cause some of them. Thus, the possibility exists that trace metal biogeochemistry may partly control the species composition found in natural biological assemblages or communities, hence trace metal ratios may serve as part of the mechanism driving Tilman's second evolutionary prediction.

This hypothesis should not be construed as excluding climatic effects upon these biological associations, especially as climate controls the potential amount and type of erosion from source material, and direct climatic effects upon biota have long been documented (i.e., Andrewartha and Birch 1954). Rather this hypothesis is focused solely upon the potential role(s) of trace

metal concentrations and ratios in shaping biological assemblages, a function supported by both the literature (i.e., DiTullio, et al. 1993, Earle, et al. 1987, Frey and Small 1980, Fuhs 1974, Lee 1983, Patrick, 1978, et al. 1969, 1975, Spencer 1980) and results from this research.

2. Based Upon Sedimentary Trace Metals and Water Column Molybdenum

a. Nickel

i. In the control of competitive success among cyanophytes. Nickel is required by algae and cyanophytes for urease (Oliveira and Anita 1984, 1986; Price and Morel 1991) and by cyanophytes (Van Baalen and O'Donnell 1978) for hydrogenase (Papen et al. 1986). Hydrogenase is required to process, or "recover," the hydrogen produced as a byproduct of nitrogen-fixation, and Ni-deficient *Rhizobium* has been shown to be a less active nitrogen-fixer (Dalton and Evans 1986, Harker, et al. 1984, Klucas, et al. 1983). Cyanophytes also apparently have a higher requirement for nickel than do eukaryotic algae (Wang and Wood 1984).

The form of sedimentary nickel which has the highest correlation with filterable Ni in the epilimnion of the summer water column of the study lakes is the "organic" fraction. The biovolumes of the bloom-forming species of *Anabaena* correlate quite well with the amount of organic Ni in the sediments (Figure 39). However, when the non-bloom-forming species of *Anabaena* are added to the regression model the coefficient of variation is reduced. This reduction suggests that the non-bloom-forming species of *Anabaena* found in Oregon either lack hydrogenase, or do not use nickel in it. Furthermore, it is possible that high concentrations of filterable Ni in the summer epilimnion of lakes with high P concentrations give bloom-forming *Anabaenas* an advantage over *Anacystis* by allowing the former genus to fix nitrogen efficiently because there is a negative relationship between nickel and the bloom-forming, but non-nitrogen-fixing, coccoid cyanophytes (Figure 40).

To verify whether or not nickel is actually a limiting factor for the growth of bloom-forming *Anabaenas*, a lake where this situation occurs naturally needs to be found and studied. Based upon this research, as discussed below, it appears that the Lava Lake population of bloom-forming *Anabaenas* is limited by nickel.

Alternative limitations on this group of cyanophytes in Lava Lake must first be eliminated as possibilities. There are four possibilities: low total dissolved P, a short retention time, cool temperatures, and another trace metal.

Figure 102 and Table 10 indicates that neither low phosphorus concentrations nor a short retention time are limiting *Anabaena* in Lava Lake.

The failure of *Anabaena flos-aquae* and/or *A. circinalis* to grow well in Lava Lake is probably not due to its thermal regime. This conclusion was reached by comparing three physical characteristics which strongly influence the annual temperature cycle in lakes, elevation, mean depth and lake volume (Table 10). The data set analyzed was restricted to those lakes in the Cascades or just east of the Cascade crest which had *Anabaena* populations. By restricting the set to Cascade and eastward lakes, it is likely that only lakes with a similar climatic regime are being compared. By dropping the lakes which lacked *Anabaena* altogether, the lakes where *Anabaena* may not occur due to some other reason are excluded from the comparison, since the objective is to determine the "relative fitness" of different lakes to support bloom-forming *Anabaena*. Six study lakes fit these criteria, three of which had higher summer densities of bloom-forming *Anabaena* than Lava Lake. The three lakes with higher *Anabaena* biovolumes per ml were Paulina (222.4), Suttle (153.4), and Todd (123.0). Lava Lake populations averaged 33.8 cubic μm per ml. The two remaining lakes, Lake of the Woods and Walton, had mean summer *Anabaena* biovolumes of 4.3 and 0.8 cubic μm per ml, respectively, and were not further analyzed.

The only lake which ought to have a more favorable thermal regime than Lava is Suttle Lake (Table 10), roughly 400 m lower in elevation though twice as deep. Both Todd and Paulina are over 400 m higher and are approximately equal to, or much deeper than, Lava. Both elevation and mean depth suggest that Lava should be warmer than Todd and Paulina. The criterion of lake volume suggests that the annual temperature cycle of Lava ought to be average when compared to the group mean. August epilimnion temperatures from Johnson, et al. (1985) are 15 °C for Todd, 16 °C for Paulina, and 20 °C for Lava. Surface temperatures from Suttle Lake of 20 °C were measured in August 1986 and 22 °C in July 1988. The Suttle surface temperatures indicate that it appears to provide a warmer environment for *Anabaena* than do the

Figure 102. Summer biovolumes of *Anabaena flos-aquae* and *A. circinalis* vs. summer epilimnetic concentrations of tdp (in $\mu\text{g}\cdot\text{l}^{-1}$).

other three lakes while the epilimnetic temperatures directly support the hypothesis that Lava is a warmer lake than Todd or Paulina. Thus, on the basis of temperature, the order ought to be Suttle, Lava, and then Paulina and Todd.

Another possibility is light limitation. This is a weak possibility as many cyanophytes possess the ability to regulate their buoyancy, and the successfulness of at least one of these species, *A. circinalis*, at buoyancy regulation is well known (Reynolds 1984). For the record, the Secchi Disk depths of these six lakes are 7.0 m for Lava, 7.0 m for Todd, 3.5 m for Suttle, 4 m in August for Paulina, 8.5 m in August for Lake of the Woods, and 2.7 m for Walton. There does not appear to be light limitation of *Anabaena* in Lava Lake.

The final possibility is limitation by a trace metal. Both iron and molybdenum are necessary for nitrogen fixation; however, as Table 10 demonstrates, bloom-forming *Anabaena* populations do not correlate with sedimentary iron in any form, nor with filterable molybdenum in the epilimnion, nor very well with either exchangeable or total available nickel in the sediments.

However, the biovolume of *Anabaena* does correlate well with the concentration of "organic" nickel in the sediments which is correlated with filterable Ni in the summer epilimnion, but not with these other parameters. This suggests first, that dissolved Ni is being taken up by these cyanophytes for use in urease and hydrogenase and that, when cells of this genus die and sink to the sediments, the biologically taken up Ni is measured in the sediments as organically-associated metal. The second, more specific, conclusion is that Ni limits *Anabaena* in Lava Lake.

Two things appear to be necessary before Ni-limitation of nitrogen-fixation by bloom-forming *Anabaena* in Lava Lake can be proven. First, the epilimnetic concentrations of filterable Fe and Ni in Lava Lake need to be determined as well as the concentrations of ammonia and nitrate+nitrite as well as verification of the fMo concentration. Second, experiments need to be performed to demonstrate that Lava Lake *Anabaena* populations grown in Lava Lake water have a suppressed nitrogen-fixing capability which nickel specifically improves.

Table 10. Selected physical and chemical parameters for four East Slope *Anabaena* lakes.

a. Physical characteristics affecting thermal regime

Lake	Elevation (m)	Mean Depth (m)	Lake Volume (cubic hm)
Lava	1445	6.0	8.94
Suttle	1048	13.5	13.79
Todd	1875	6.4	0.75
Paulina	1930	49.7	308.07

b. Water chemistry (N.D. - Not Determined)

Lake	tdP(μ g/l)	diN(μ g/l)	fFe	fMo	fNi
Lava	530	N.D.	N.D.	5.20	N.D.
Suttle	40	120	27.0	1.34	19.0
Todd	63	330	N.D.	4.20	N.D.
Paulina	32.5	160	255.5	8.65	19.5

c. Sediment chemistry

Lake	FeEx	FeOr	FeTA	NiEx	NiOr	NiTA
Lava	181	28.1	489	3.88	0.00	3.88
Suttle	219	26.7	1320	11.6	7.64	30.1
Todd	8270	2490	108000	15.6	19.4	50.2
Paulina	68.8	117	86400	9.47	25.4	105

tdP = total dissolved phosphorus (from Johnson, et al. 1985)

diN = dissolved inorganic nitrogen (ditto) = NH_3 and $\text{NO}_2 + \text{NO}_3$

fFe = filterable summer epilimnetic Fe in nmol/l (R. Collier unpublished data)

fMo = filterable summer epilimnetic Mo in nmol/l (R. Collier; this research)

fNi = filterable summer epilimnetic Ni in nmol/l (from Bob Collier's work)

ii. Relationships with freshwater diatoms. A number of correlations were found between a number of sedimentary diatoms and ratios which involved nickel. However, only two sets appeared to have physiological explanations. Both *Stephanodiscus niagarae* and *S. alpinus* demonstrated the same non-linear negative pattern with organic Ni in a ratio (Figures 97 and 98), though neither possessed a strong direct relationship with it. The relationship between *S. niagarae* and the NiOr:N ratio suggested either that Ni is relatively toxic to *S. niagarae*, that this species lacked the Ni-containing enzyme, urease, or that *S. niagarae* had a relatively high P requirement in comparison to its nitrogen requirement. Since *S. alpinus* had a similar relationship, though with organic Mn instead of nitrogen, and since it seemed to be a fall-winter species in Oregon lakes rather than a spring-summer form, the lack of urease in species which grow best in the absence of grazers made physiological sense.

The strongest correlation between sedimentary nickel and relative numbers of diatom frustules in the sediments was with *Epithemia muelleri* and two ratios involving organic Ni. *E. muelleri* displayed a clear Gaussian curve in response to the ratio of organic Ni to Co, with an optimum between 1:1 and 1.5:1 (Figure 73), as well as a positive correlation with an increasing ratio of organic Ni to total available nitrogen. When plotted in a three-dimensional graph, the latter correlation between organic Ni and nitrogen was revealed to be a threshold phenomenon instead of a simple positive correlation as only three null samples from Eel Lake intruded into the area where the high values occurred. This pattern suggested that the optimal niche of *Epithemia muelleri* was restricted by the interactions of these three parameters.

The physiological basis for the observed interactions is not a simple or clear one. Although *Epithemia muelleri* is generally considered to be an epibenthic diatom, the weak positive organic Ni to total available nitrogen relationship suggests that this species utilizes urease to obtain nitrogen from animal wastes as a major nitrogen-uptake route. Although initially this seems difficult to accept, the best alternative is involvement of Ni in another, presently unidentified, enzyme within the nitrogen assimilation and/or utilization pathways. The near-unity optimal ratio between organic Ni and Co suggests a role for vitamin B₁₂ either in the structural stability or detoxification of the intra-

cellular pool of Ni, or as part of the same pathway. While such a physiological relationship has not been described in the literature, the clear relative success of *E. muelleri* at a ratio of Ni:Co near 1:1 suggests such a linkage, possibly structurally within the same enzyme, or more likely, in the same pathway.

The 1:1 stoichiometry of organic nickel to cobalt characterizing the optimal relative abundance of *Epithemia muelleri* can not be regarded as merely an interesting coincidence lacking physiological significance because this pattern, with a similar or the identical optimum, was repeated in varying degrees for 14 other species of the 46 taxa of sedimentary diatoms examined. (As might be expected from the strong Co and Ni results obtained during the MLR, *Asterionella formosa*, after exclusion of Paulina Lake values, is one of these species.) Thirteen more may also possibly possess this feature while yet another species (*Cyclotella meneghiniana*) demonstrated an optimum at 2:1. Three of the other diatoms clearly having the 1:1 pattern, *Navicula cryptocephala*, *Nitzschia amphibia*, and *N. frustulum*, are shown in Figures 103 and 104 for verification. The taxonomic width of distribution among the different species apparently possessing this characteristic ranges from *Fragilaria capucina* and the sole *Eunotia* studied through the melosirids and several species of thalassiosirids. The only orders studied which lacked representation were the Achnanthes and the Surirellales. Furthermore, this pattern was present in both planktonic and epibenthic diatoms. As seventeen species, including some very common ones such as *Achnanthes minutissima*, and *Stephanodiscus hantzschii*, lacked any relationship with the ratio of organic nickel to cobalt and as this ratio varied from 0:1 to over 10:1, it is clear that this is a phenomenon which may be an important factor influencing the distribution of some diatoms. Thus, despite lacking a known physiological relationship between these two trace metals, it should be concluded that the observed relationship between organic nickel and cobalt for *Epithemia muelleri* was not accidental. Further investigation is recommended.

b. Vanadium as a major factor influencing phytoplankton distribution. The importance of vanadium in controlling the species composition, relative abundance, and growth of phytoplankton has been underestimated by most limnologists, with Patrick (1978, et al. 1975) and Lee (1983) the only others

Figure 103. Relative sedimentary remains of *Navicula cryptocephala* (in percent of total composition) vs. the organic Ni:Co ratio.

Figure 104. Relative sedimentary remains of *Nitzschia amphibia* and *N. frustulum* (in percent of total composition) vs. the organic Ni:Co ratio.

who clearly identified its large impact upon natural assemblages. The broad, species-specific, confirmation of this metal's role in influencing the relative abundance of phytoplankton species is one of the two most significant discoveries of this research and has potentially serious environmental consequences. The key characteristic of vanadium with respect to phytoplankton is that most species appear to have a narrow optimal range of acceptable concentrations (Lee 1983), a range which is exceeded by its variability in the natural environment. An example of this phenomenon, though low in numbers of values, is *Staurostrum gracile* vs. total available sedimentary V (Figure 29); the sole null value within its optimal range is Lake Oswego, apparently resulting from its response to the high Cu concentration in that lake (Figure 30). A second example is the numerous cases of monotonic increase or decrease by different species of phytoplankton or sedimentary diatoms with increasing concentrations of different extractions of or ratios involving sedimentary V. These include the summer populations of *Cyclotella stelligera* (Figures 21 and 22) and *C. radiosa* (Figure 23), *Ankistrodesmus falcuatus+spiralis*, *Sphaerocystis schröteri* (Figure 34), and the relative sedimentary numbers of three *Fragilaria* species (Figures 47 through 50), *Cocconeis placentula* (Figure 62), *Nitzschia amphibia* (Figure 74), *Cyclotella krammeri* (Figure 85), and *Cyclotella dubius* (Figure 90), as well as possibly *Melosira italica* and *Stephanodiscus hantzschii* (Figures 82 and 94). Unlike the situation for zinc these monotonic or Gaussian changes suggest that there are no species-specific physiological specializations with regards to affinity, uptake or storage mechanisms. Passive transport, or diffusion through the cellular membrane, seems to account for all V uptake by most species of algae and cellular accumulations are probably proportional to the environmental concentration that the cell is exposed to. Such a simple mechanism is advocated because aqueous V is normally an anion instead of a cation (Lee 1983, Wehrli and Stumm 1989), and is relatively soluble and usually non-limiting (Lee 1983). The anionic nature of dissolved V may also cause the inability of many phytoplanktonic species to detoxify this metal as all metals with known bacterial or algal detoxification mechanisms are cations (Wood and Wang 1983).

The environmental impact of vanadium is not related to changes in total lake productivity; instead, it seems to produce species changes in

phytoplankton assemblages (Lee 1983). Without species-specific phytoplankton identifications, this effect has been almost completely missed. This research verified Lee's contention through the examination of Woahink Lake phytoplankton populations and sediment data. Since V is a common pollutant resulting from petroleum combustion (Charles and Norton 1986, et al. 1987, 1990; Lee 1983), its effects may already be widespread throughout lakes in the developed world.

The presence of *Cyclotella stelligera* was cited by Johnson, et al. (1985) as partial justification for classifying Woahink as oligotrophic conditions, yet its relative abundance in the sediments, already the most abundant species, increased by over a third between the lower strata and the 2 cm depth ($17.9\% \pm 2.3\%$ vs. $25.3\% \pm 0.0\%$). This lake has also demonstrated signs of increased eutrophication over the past 20 years (Daggett 1994). At the same time as *C. stelligera* was increasing, the relative amount of V in the sediments also increased as demonstrated by the vertical profiles of V and the V:Al ratio (Figures 9 and 15). This V increase was probably due to increase petroleum combustion downwind from the lake (section IV.B.4.b). Increased numbers of *C. stelligera*, in slightly brackish waters ($>5 \text{ mg Cl}\cdot\text{l}^{-1}$), were found to correlate with the sedimentary concentration of organic V (Figure 21) as well as the ratio of exchangeable V:Cu (Figure 22). Thus, the following chain of logic appears to be a valid description of the current situation in Woahink Lake: Under the right environmental conditions, *C. stelligera* flourishes with increasing amounts of V; increasing quantities of this metal are being added by auto exhaust, etc. to Woahink; consequently the predominance of *C. stelligera* in this lake may be strengthened as demonstrated by the increase in its relative sedimentary abundance. Yet, as Daggett (1994) observed, there has been little increase over the past 20 years by primary productivity in this lake. The apparent increase in *C. stelligera* in Woahink seems to be matched by reductions in cell numbers and species-specific primary productivity of other, less V tolerant, species of phytoplankton, or of species which require less V than *C. stelligera*.

The apparent phytoplankton species shift due to V pollution in Woahink raises several important general environmental issues. First, what other subtle shifts are being missed by neglecting species-specific identification in favor

of limiting aquatic ecosystem analyses to just standing stock estimates (i.e., chlorophyll a measurements) and primary production? The conclusion reached in section IV.B.2 that changes in trace metal concentrations are not correlated with trophic status or changes in primary productivity implies that trace metal effects may not be detected, except at the gross pollution level, by just measuring primary production rates. The recent observation that iron is limiting in the world ocean only for the larger diatoms (Chisholm and Morel 1991, Hutchins, et al. 1993, Kerr 1994) is an excellent example of the shift in thinking on such problems that is required. Second, are there any cascade effects of V pollution-driven shifts at higher trophic levels? Third, is V an isolated instance, or are there other trace materials causing similar effects? At least one other trace metal, selenium, may possibly produce such shifts (Lindström 1983, 1985, Nriagu and Wong 1983, Patrick 1978, Stephan, et al. 1986); one substance might just be an oddity, the existence of two suggests possibly another set of environmental problems may be occurring. And, as a more specific response to this particular case, given these findings, can *C. stelligera* still be used as indicator of oligotrophic conditions? Without regular testing for environmental V concentrations, which is not an easy task, the validity of this categorization appears doubtful. Finally, how widely distributed might phytoplankton species shifts due to vanadium pollution be?

c. Zinc as a limiting trace metal in fresh water

Zinc is required for silicate metabolism in diatoms (Rueter and Morel 1981) and a significant amount of zinc cycling in Windermere is driven by the spring *Asterionella formosa* bloom (Reynolds and Hamilton-Taylor 1992). Zinc has been determined to be a limiting nutrient for diatoms in the ocean (Brand, et al. 1983, Bruland 1989, Sunda 1988, Sunda and Huntsman 1992) to such a severe extent that cadmium, a normally toxic metal, is used to substitute for it by at least one species of diatom (Price and Morel 1990). There has been no specific evidence reported in the literature to date to support a similar limitation in freshwater, however this research suggests that zinc may limit the growth of some of the larger and/or more heavily silicified freshwater diatoms. There was no conclusive evidence found to support zinc limitation of any other division of freshwater phytoplankton however. (The sole correlation observed

between zinc and a non-diatom, the green alga, *Scenedesmus denticulatus* was a weakly (due to the low number of data points) negative one. If it is valid, then it may be reflecting competition between *S. denticulatus* and a species of diatom (or several of them) instead of a direct inhibition by zinc.)

The first piece of evidence supporting zinc as possibly limiting diatoms in freshwater was the fact that the majority of correlations observed between diatoms and Zn were with the organic form of Zn, suggesting that the Zn was probably originally assimilated by living organisms. This assumption is supported by Collier and Edmond's (1981) model for Zn flux to the sediments, Reynolds and Hamilton-Taylor (1992) data on Zn transport by *Asterionella formosa* in Windermere, and Balistrieri, et al.'s (1992b) observations of Zn cycling in Lake Sammamish. Although under anoxic high sulfide conditions some dissolved Zn in lakes precipitates as zinc sulfide, it is probable that most of the peroxide-extracted Zn measured here, with a few notable exceptions, was truly organic Zn due to the oxidizing which occurred during the stirring of the exchangeable extraction. Thus, the peroxide extraction seemed to mainly measure Zn which had once been incorporated into living cells. Since most of the correlations were between organically-originated Zn and diatoms, this indicated that the abundance of this division might be partially controlled by water column Zn concentrations. Consequently the likelihood for Zn limitation of diatoms in freshwater was an implicit possibility, supported by the data from marine species.

The clearest proof for probable Zn limitation of freshwater diatoms is demonstrated by *Synedra radians*. The absolute abundance of this species in the water column is strongly and positively correlated with the ratios of organic Zn to organic Fe and Co, yet relative numbers of *S. radians* frustules in the sediments drops from a rather high percentage (>17%) at low concentrations of sedimentary organic Zn (<2.5 ppm) to a constant 2-3% of the total frustule count above that concentration. Initially this decrease seems counterintuitive as this diatom increased in absolute numbers with increasing amounts of organic Zn. However, upon reconsideration, there is a logical mechanism for this contradiction and it indicates support for the idea of Zn limitation. First, the relative decrease of *S. radians* in the sediments is not a classic competition response to a limiting nutrient as illustrated in Tilman (1982) and in earlier

work, although such a pattern with respect to sedimentary organic Zn was found in the distribution of both species of *Amphora* studied. In the case of *S. radians*, instead of the gradual decline demonstrated by *A. ovalis* and *A. perpusilla*, there is a clear threshold concentration above which the significance of this species drops to a more-or-less constant value. Second, it is not a toxic response because this species persists, though in reduced numbers, as a stable percentage far above this threshold. The probable explanation, if the amount of water column Zn available to phytoplankton is proportional to the concentrations of sedimentary organic Zn, comes from Sommer (1985)'s model for algal adaptation to nutrient limitation. According to Sommer there are three possible strategies for algal adaptation to nutrient limitation, velocity, affinity and storage specialists. Based upon Figure 51, *Synedra radians* is an affinity specialist, as it apparently does well relative to other diatoms at low Zn concentrations. Although it also grows at higher concentrations, there appear to be other diatoms which are velocity specialists in regards to Zn uptake so they grow even faster at higher concentrations. Consequently the relative numbers of *S. radians* drop as the Zn concentration increases. However, because the velocity specialists can not assimilate Zn below a certain concentration, there is always a period of time when the high-affinity strategy of *Synedra radians* allows it to grow under conditions of reduced competition for dissolved Zn. Furthermore, if this diatom produces organic molecules similar to siderophores which enable it to assimilate Zn better, or if it has a small but efficient Zn storage system, and/ or a Zn-"recycling" mechanism, then *S. radians* can persist, though in lower numbers, at the higher concentrations required by the velocity specialists.

The *S. radians* example presents indirect, but strong, evidence for general Zn limitation of diatoms in freshwater ecosystems as revealed by the presence of a clear shoulder in *S. radians* abundance at a sedimentary organic Zn concentration of 3 ppm by dry weight. The shoulder indicates that there is a sharp reduction in competition for that metal below that concentration. This concentration is apparently a threshold value of sedimentary organic Zn for most diatoms, and suggests that most species can not assimilate it below a water column concentration which produces that sediment concentration. This finding

implies that many freshwater diatom species will probably be determined to be Zn limited.

While *Synedra radians* is perhaps the best example found here of an affinity specialist, there were both several other affinity specialists as well as diatoms which clearly demonstrated velocity and storage specializations. *Achnanthes minutissima* had a clear shoulder in the organic Zn:Co ratio, suggesting affinity specialization. *Navicula viridula* was definitely another affinity specialist, and *Nitzschia dissipata* may have been yet another one though there was less data available to confirm this evaluation. *Cyclotella radiosa* was clearly a velocity specialist as its plot with the OrZnV ratio demonstrated (Figure 86). (The best predictor of the relative sedimentary abundance of *C. radiosa* was the relationship between the OrZnV ratio and this diatom. This result, in combination with the weak summer correlation with V, suggested that both trace metals may be important factors limiting the relative success of this species.) *Surirella linearis* may also be a Zn velocity specialist. The two *Amphora* species studied are examples of large, relatively heavily silicified, diatoms which are apparently not good competitors for Zn, suggesting a low maximum assimilation rate. Since they are benthic forms, they may obtain it from the sediments, so probably do not require a high number of uptake sites either. The gradual decline in the relative abundance suggests that these diatoms store this metal moderately well, so may only gradually be replaced by benthic velocity specialists.

Although the best correlation for *Melosira ambigua* clearly demonstrated that it was another velocity specialist, limited by the ratio of zinc to cobalt (Figure 81); two features suggested that something else more complicated was occurring. First, the best fit was with the total available forms of these two trace metals, not the organic nor the exchangeable fractions. Second, there was the presence of a distinctive subset of lakes, those of the Willamette Valley, which equally clearly lacked this relationship. While Clear and Oswego possessed higher than average ZnTA, neither had abnormally high values and Co concentrations in both lakes were quite average. One hypothesis for the observed differences is that they were due to possible enumeration and/or identification errors consistent only within these two lakes. Alternatively, something else may be limiting this species in these lakes (and in the other

western Oregon lakes where it occurred), but that this ratio is still the most important limiting factor for this species in lakes of the Cascades and Eastern Transition ecoregions. However, a third hypothesis is more likely that either of these to have caused the difference. Airborne Zn pollution is widespread in western Oregon, but less so in the non-industrialized mountains (Dunnette 1983), while Co is not a common pollutant in aqueous systems anywhere (Förstner and Wittman 1979). The extra particulate Zn in the airshed of the Willamette Valley would bias the total available Zn:Co ratios in Clear and Oswego Lakes, and shift the relationship between *M. ambigua* and ZnTA in the direction observed.

The cause for *M. ambigua* correlating best with the ratio of total available metals rather than the ratio between the metals in the organic fraction was not determined. One hypothesis is discussed here. The major source of sedimentary Zn has been demonstrated to be algal uptake of dissolved Zn, followed by transport of cells to the sediments (Balistrieri, et al. 1992b, Collier and Edmond 1981, Morfett, et al. 1988, Reynolds and Hamilton-Taylor 1992, Salomons and Mook 1980, Sigg, et al. 1987). Sedimentary Zn has been found to absorb onto iron hydroxides (Johnson 1986) although redox processes do not drive this absorption, nor cause any deabsorption (Morfett, et al. 1988). One cause for these transformations in superficial sediments may be bacteria as occurs with Mn and Co (Balistrieri, et al. 1992, Chapnick, et al. 1982, Kepkay 1985). Consequently, it appears that when cells of *M. ambigua* die, they may quickly lyse, releasing their intracellular organic Zn. If the dying cells have already sunk to the sediments or have earlier attracted a population of epialgal bacteria, then the organic Zn compounds are probably consumed by bacteria for the energy present in the organic part of these compounds, and afterwards the extra Zn is excreted by the bacteria, then absorbed by the iron hydroxides adjacent to the bacteria in the sediments. Verification of this hypothesis is required however.

d. The lack of iron results

There were several interesting findings concerning iron and the different species of summer phytoplankton and sedimentary diatom frustules studied here, but when compared to the number of correlations found with either

nickel, vanadium, or zinc, the frequency of interesting findings involving this trace metal was quite low. Before this research began, it was hypothesized that iron would be a very important limiting trace metal. The results here do not support that hypothesis. The relative insignificance of iron as a limiting trace metal for phytoplankton growth in these lakes is the topic of this subsection. (The more interesting findings are, however, summarized at the end of this section.)

The relative scarcity of significant iron findings may have been due to one or more possible causes. The first possibility is that the partial chemical transformations that occurred during the extractions obscured the interactions present between iron and the different species of phytoplankton and benthic diatoms. This, however, is not likely for reasons to be discussed in the following three paragraphs. The primary alternative to this possibility is that there was an actual lack of findings. But if so, then the question becomes what caused such a lack, especially since iron is known to limit phytoplankton growth in the ocean (Chisholm and Morel 1991, Hutchins, et al. 1993, Kerr 1994) and has been suggested to be an important limiting trace metal in some lakes (Rueter and Petersen 1987, Wurtsbaugh and Horne 1985). There are at least two different mechanisms which could explain this scarcity of positive findings. One possible cause is that there were few or no species and/or lakes studied for which or where iron was an important limiting nutrient. The other possible cause is that iron in freshwater always (or universally) limits the growth and reproduction of phytoplankton due to its relatively unique aqueous chemistry.

That some chemical transformations occurred during the extraction process is not at question. As documented by Rapin, et al. (1986) there should have been a loss of exchangeable iron and an increase in iron oxides due to oxidation of reduced iron in the pore waters. Also there would have been a loss of iron sulfides from the peroxide extraction due to mixing during the exchangeable extraction phase, again into a form of iron oxide. However, neither Rapin, et al. nor this study noted any oxidation of iron, or of any other metal, associated with organic material either by mixing or, to any significant extent, through drying. This strongly suggests that the peroxide extraction of iron is mostly organic in origin together with some of the less easily-oxidized sulfides. Thus, it seems highly probable that the amount of organic iron present was

actually relatively accurately assessed. Furthermore, as correlations with summer phytoplankton and sedimentary diatoms were found involving both other metals in the organic fraction as well as, though less frequently, iron in the same fraction, this makes it probable that what correlations to be found with organic iron and phytoplankton, given the limitation of sample size, were observed.

Although there were probably significant amounts of iron transformed from soluble forms in the exchangeable fraction to solid amorphous iron oxide, this is less of an important restriction on the validity of the data than would appear at first glance. To begin with the extraction conditions for the exchangeable fraction were the least variable of all four extractions, mixing for half an hour, then centrifuging for two, so the total amount of time before acidification, hence stabilization, was less than 4 hours, thus significantly reduced the amount which would have changed form past the initial oxidation event. Consequently the amount of iron transformed from the exchangeable phase into an oxide should have been proportional only to the amount present. As the degree of variability in exchangeable iron concentrations was greater than two orders of magnitude, this implies that which lakes had high FeEx concentrations and which did not were probably real, even if the absolute concentrations were not accurate. Therefore, despite the loss of exchangeable iron into a form of FeOx(s) during the extraction, relative relationships ought to have remained, hence, if there were any correlations between exchangeable iron and the different phytoplankton species, it should have been detected, even if the specific coefficients were wrong. Furthermore, there were some correlations between exchangeable iron and several species of summer phytoplankton and sedimentary diatoms observed, indicating that such could be detected.

A secondary line of evidence supporting a lack of extraction influence upon the near-absence of significant iron correlations is that there was only one correlation found between total available iron and a biological taxon. This means either that there weren't any significant ones completely lost in the extraction procedure, or more likely, that the amount of sedimentary iron oxides due to non-biological activity swamped the increase due to the transformation of the exchangeable and sulfide forms of iron into oxides. However, since some were

found with all three forms of iron examined, the latter possibility only means that just the weaker ones were lost.

The possibility that none of the lakes examined were iron limited is conceivable as only Blue, Lava, and Crater are clearly nitrogen-limited. Mulvey (1986) did not find strong evidence for iron limitation in Blue Lake, and data presented here suggest that Ni is probably more important than iron in Lava Lake, which leaves only Crater among the lakes of this study as potentially iron limiting, a lake possessing relatively high sedimentary Fe concentrations. Therefore, a lack of Fe limitation in the study lakes must be regarded as a valid possibility.

The possibility that none of the analyzed species were limited by iron may be rejected as a valid explanation based upon the following rationale. The chrysophyte nanoflagellates are known to possess very high requirements for iron (Sandgren 1988), and other phytoplankters are believed to possess similarly-sized requirements (Raven 1988). All analyzed chrysophytes demonstrated clear secondary correlations with one of the forms and/or ratios involving iron. The selection of species to be analyzed was made before reading Sandgren (1988), therefore inclusion of the chrysophytes served as a "blind" comparison. Finding Fe limitation of these organisms indicated both that the analytical system used to detect correlations between iron and different phytoplankton species measured real limitations by this metal, and there were species present which were clearly limited by iron.

The final possibility for the observed lack of iron limitation is the nature of the aqueous chemistry of this trace metal. First, it is much less soluble in oxygenated water than Mn, Cu, Zn, V, and apparently Co. Manganese has been long known to be more soluble than iron (Delfino 1968); the photoreduction of manganese oxide by sunlight (Sunda and Huntsman 1985, 1988) is probably a partial cause for this difference. Another cause is that specific aquatic bacteria which mediate most of the precipitation of both Mn and Co may not be very common in some lakes, particularly oligotrophic ones (Sigg, et al. 1987). Also lessening the impact of low concentrations of soluble Co is the low requirement that most species have for this metal. Most dissolved Zn is present in the form of organic complexes (Balistrieri, et al. 1992b, Bruland 1989) which maintain a relatively stable concentration of it in the water column. Copper

solubility is also largely controlled by the presence of dissolved organic materials which form complexes with it (Allen, et al. 1970, Coale and Bruland 1988, McKnight 1981, Wagemann and Barica 1979, Wilson 1978). In combination with the very low requirement of phytoplankton for this trace metal, this means that Cu deficiency, like that of Co, is not likely to be found. Since Ni is not known to be used by phytoplankton other than for urease and hydrogenase, the circumstances under which low Ni concentrations could have widespread significance ought to be rather rare as well, with the two exceptions discussed above. The physiological needs for both V and Mo are also quite small when compared to their solubility products in pH neutral waters. Consequently, in comparison with iron, all seven other metals studied here have an absolute solubility higher than iron, or the phytoplankton have a lower requirement for them than their maximum solubility product, or both.

Iron, on the other hand, does not form complexes with organic materials other than humates and no humic lakes were studied here; its inorganic solubility products are very low and these compounds are not sunlight sensitive; and most organisms possess a high requirement for it (Hutchins, et al. 1988). This suggests that aquatic organisms have been selected for efficient iron utilization since the cyanophytes first produced an oxygenated atmosphere about 2 billion yrs BP, which implies that the organisms present in a particular aquatic environment whether it be a hypereutrophic lake, a humic acid lake, or the blue water parts of the world ocean, have been strongly selected for the prevailing iron concentrations of that environment. Since other resources are usually the primary limiting factors in such environments, iron limitation will probably be obscured by the requirements for these other nutrients. Therefore, iron limitation should only be observed either in environments when the predominant limiting nutrient for that environment has been replaced by a different one such as in ultraoligotrophic, high P lakes, or in the relatively few species which are specialized for "intermediate" environmental conditions (Sommer 1993) or possess size limitations such as the large "blue water" marine diatoms (Chisholm and Morel 1991, Hutchins, et al. 1993, Kerr 1994).

An additional aqueous chemical mechanism for possibly explaining the observed lack of iron limitation in some lakes is the "Ferrous Wheel" cycle of Campbell and Torgersen (1980). This cycle provides a way to refresh dissolved

and colloidal iron concentrations in anoxic lakes, hence possibly making iron limitation rare in such waters. Such a cycle is not present in the ocean, which implies that freshwater phytoplankton have a greater possibility of obtaining iron than their marine counterparts. While this may be a valid explanation for differentiating between the ocean and some lakes, the problem with it here is that, except for Oswego, there were no lakes in this study with anoxic hypolimnions to drive the “Ferrous Wheel”.

In conclusion, there are two likely possibilities for causing the relative absence of iron limitation observed in these lakes. The first is a possible lack of iron limited lakes among those sampled. The second possibility is that iron limitation can only be detected in freshwater under unusual circumstances for a relatively few species due to the insolubility of iron in oxygenated waters which causes a nearly uniform lack of iron availability in all lakes.

Having said this, nonetheless, iron is still a relatively important trace metal for the investigated organisms. It is clearly more important than Cu or Mo (though Cu demonstrates quite distinctive ecological impacts, mostly due to its addition to Oswego) and is more frequently limiting than either Mn or Co (as discussed in the next section). All clear relationships between sedimentary Fe and various phytoplankters and epibenthic diatoms, with one exception, demonstrated positive correlations. This suggests that for these organisms Fe is a limiting nutrient in short supply. In the summer phytoplankton, besides the chrysophyten nanoflagellates, there was a positive correlation between *Oocystis lacustris* and organic Fe. In the sediments, positive linear correlations were observed for *Synedra ulna* with FeEx:N, *Achnanthes linearis* with FeEx:P, *Pinnularia microstauron* with FeTA:P, and *Stephanodiscus hantzschii* with FeOr:N, as well as a non-linear one between the OrZnFe ratio and *Synedra radians*. The only negative relationship observed with iron was a non-linear one between *Navicula viridula* and the FeOr:P ratio (Figure 67), possibly due to coprecipitation of phosphorus by iron making P unavailable to this species.

e. The limited functions of cobalt and manganese

While cobalt, either in the elemental form or as vitamin B₁₂, is universally required by plants and phytoplankton (Patrick 1977, Salisbury and Ross 1969, Reynolds 1984), there is little published evidence to support widespread Co

deficiency in nature. The findings here support this observation. Although a number of ratios were found which involved Co, upon closer examination most of them demonstrated limitation by the other trace metal in the ratio. The near-absence of variability in the different fractions of sedimentary Co, when compared to that of other trace metals, supported the relative biological insignificance observed. Thus the sedimentary concentrations of different Co extractions mainly appeared to be index conditions, or reference levels, for the mineral nutrition of the species of phytoplankton or sedimentary diatom studied.

Nonetheless, there were a few exceptions found in this analysis which might be worth further examination. Apparent Co limitation was observed for the absolute summer cell densities of *Asterionella formosa*, *Chlamydomonas* sp, and *Mallomonas* spp, as previously hypothesized by Sandgren (1988), as well as in the summer biovolumes of *Synedra ulna*. The positive correlations between the relative sedimentary abundances of *Navicula cryptocephala* and possibly *Cyclotella stelligera* to the organic Co:P ratio also suggested that these two species may also possess a high requirement for Co, or possibly vitamin B₁₂, relative to other diatoms. Several species of *Melosira* may require vitamin B₁₂ as well, though the supporting evidence is weaker. Although there is little evidence Co limits growth by phytoplankton as an assemblage; species-specific needs may be a different situation. These taxa might be good candidates for an evaluation of this possibility. However, since this research found no evidence to support the idea that this trace metal is limiting in Oregon, future field work probably should not be done here but where there have been Co deficiencies found through agricultural research, such as in New Zealand.

Manganese, like Co, was more notable in its non-limitation of phytoplankton than as an important deficiency or toxicity in the study lakes. This may be related to its relatively high availability as a dissolved cation and its interactions with aquatic bacteria. Also half of the significant findings were biased by the poor sedimentary diatom data from Loon Lake, further weakening any general conclusions about this metal. Unbiased Mn-limitation was only clearly observed for *Gomphonema* species other than *G. subclavatum* and for *Achnanthes lanceolata*. In both situations the key Mn fraction was the exchangeable portion, it was relative to Co, and the species involved were epibenthic.

Interestingly the best correlation for *Achnanthes lanceolata* is with the ratio of exchangeable Mn to organic Co, not OrMnCo nor ExMnCo.

Since the exchangeable Mn fraction is frequently the largest one in lake sediments unlike that of other trace metals; and is presumably more readily available than are other fractions, the fact that only epibenthic species are associated with sedimentary Mn suggests that these species may require more Mn relative to other diatoms. This may be due to one of several possibilities. These species may not assimilate elemental Co at all; instead they could be utilizing Co already transformed by sedimentary microorganisms, and so avoid the metabolic cost having to process elemental Co into a usable form, or of maintaining a large intracellular Co pool. Alternatively, occupation of the epibenthic habitat may require these species to have more Mn, and the ratio with Co may be just another example of Co serving as a reference point relative to other trace metals. A third possible explanation for these correlations is that these diatoms are limited by another resource which simultaneously restricts the bacteria which transform Mn, though this is not the most parsimonious explanation. Further studies are needed before any of these ideas can be considered to be more than just hypotheses.

f. Copper tolerant species

Only two positive correlations between an alga and organic copper were found in the summer phytoplankton studies, *Selenastrum minutum*, which belongs to a genus known to have a very high Cu tolerance (Wood and Wang 1983), and *Oocystis pusilla*. *O. pusilla* was also an apparently highly tolerant green alga because, like *S. minutum*, it attained its highest summer populations in Lake Oswego during the period of Cu additions. Recent evidence (Xue and Sigg 1993) indicates that some green algae release sulfidic proteins in response to added Cu and that these proteins specifically bind to free Cu in fresh waters, forming non-toxic organic Cu complexes; both algae observed here to be Cu tolerant may be able to do likewise.

The copper tolerance of *Selenastrum minutum* is a significant finding since a related species, *S. capricornutum*, is used by the EPA as a standard test species in their algal assay procedure (U.S. EPA 1971). The Cu tolerance reported here indicates that, through their use of *S. capricornutum*, studies which follow

the EPA protocols might underestimate the impact of Cu upon natural phytoplankton associations with potentially serious consequences for environmental impact assessments. Fortunately, the specific role of Cu as a toxic heavy metal is well documented so the particulars of this situation are not troublesome, but this finding raises the question of what other heavy metal tolerances do members of this genus have? If Wood and Wang (1983)'s detoxification mechanism works for all metals for all species of this genus, then heavy metal tolerances may have set too high under some circumstances.

There were only four minor correlations between copper and sedimentary diatoms found, three of them positive. Both *Gomphonema subclavatum* and *Epithemia turgida*, showed increased abundances with increasing concentrations of total available and of exchangeable Cu (and the organic Cu:N ratio), respectively. As these regressions were primarily controlled by Crater Lake data, a conservative interpretation of these results is required. The safest one is to assume that these two species have either an increased Cu tolerance or some means of detoxification.

The third positive copper correlation with sedimentary diatom remains was a secondary one, after alkalinity, between the relative abundance of *Nitzschia frustulum* and total available Cu, again dominated by data from Crater Lake (though data from Walton Lake supported this finding). Although caution is essential, the data for this species (Figure 77) could be described as having a crude Gaussian distribution. This suggests growth by this species may be limited at water column Cu concentrations which produce sedimentary values for total available Cu below 45 ppm. Nonetheless, based upon the data, some sort of Cu tolerance mechanism appears likely to exist in this diatom as it grows better than its competitors at higher concentrations. The reduction in growth at low Cu concentrations may be due to this mechanism interfering with Cu assimilation. One possible explanation might be a detoxification mechanism which blocks copper at the cellular membrane uptake ports, so higher external concentrations are required to overwhelm the protecting mechanism.

The final copper correlation found among diatom remains in the sediments is a negative one between *Cyclotella stelligera* and the exchangeable Cu:V ratio. This finding supports other results reported here. First, V was already known to be strongly and positively correlated with the absolute summer

abundances of this species, and second, Oswego was the only western Oregon lake sampled with a chloride concentration above 5 mg·l⁻¹ which lacked *C. stelligera*. This relationship simply indicates that *C. stelligera* correlates positively with V and negatively with exchangeable Cu.

In summary, four of the five positive copper correlations with phytoplankton and sedimentary diatoms can best be explained by invoking an increased tolerance to copper rather than a need-based limitation, while the fifth may be demonstrating limitation due to a possible detoxification mechanism. Further studies on the mechanisms of Cu tolerance involving *Selenastrum minutum*, *Epithemia turgida*, and *Nitzschia frustulum*, might be worthwhile.

g. Percent organic material

A number of species of sedimentary diatoms demonstrated primary correlations with the percent organic material in the lake sediments. The percentage of sedimentary organic material can perhaps best be thought of as an approximation of the amount of productivity occurring within a lake and its watershed (Håkanson and Jansson 1983). While most of these correlations were positive, suggesting increased capacity for growth with increased trophic state as indirectly indicated by this parameter; not all of the correlations were positive. One in particular, *Amphora perpusilla*, was negatively correlated, although the other common species of this genus, *A. ovalis*, was positively related to the percentage of organic material in the sediments. The inverse relationship between these two species based upon their correlations with the percentage of organic material suggests that competitive replacement is occurring between them, based upon lake productivity. This hypothesis is supported by the fact that the second most important correlation for both species is with organic zinc and the correlation for both takes a similar form, indicating a very similar physiological need for this metal, quite possibly an identical cellular requirement.

A second noteworthy set of correlations involving the percentage of organic material and a set of related species is that of the three common small species of *Stephanodiscus*, *S. hantzschii*, *S. minutulus*, and *S. transylvanicus*. As previously described, this triplet also includes a second important independent parameter common to all three, the percentage of carbonate. The fact that a

second chemical parameter was necessary to distinguish the niches between these three species is not surprising as there is little else to distinguish them physically or apparently physiologically. These three species support Sommer (1993)'s findings that no two phytoplankton species have exactly the set of requirements despite living in a "homogeneous" environment. Thus, given the productivity condition and concentration of alkalinity, only one of these three species should be expected to be dominant in a lake in the "small *Stephanodiscus*" niche. Both of these examples are also very good, though indirect, real world verifications of the resource ratio hypothesis of Petersen (1975), Tilman (1982), and Sommer (1989, 1993).

An interesting, though not critical to this research, observation relating to the significance of the percentage of sedimentary organic material is that it also serves as an indicator of lake productivity for fall-winter species when turbulence and light limitation might be expected to be more important primary independent variables. *Tabellaria fenestrata* is an example of such a pattern.

h. Conservative dissolved ions

Correlations between the conservative water column parameters and the different primary producers were largely absent with two exceptions, chloride concentration and alkalinity. Alkalinity was only significant for one species, *Nitzschia frustulum*. However, the cause for this phenomenon would be an intriguing one to solve. First, is it actually alkalinity as it seems to be from these analyses, or was this correlation just due to sample size? Second, is the restriction of *N. frustulum* to low alkalinity lakes due to a chemical exclusion or to competitive exclusion? Confirming the first and answering the second question could be a useful research investigation in chemical ecology which might shed some new light on the findings of Rippey and Gibson (1984).

Chloride was the only conservative aqueous ion which was the primary independent variable for more than one biological taxon. Three different species of centric diatoms, *Coscinodiscus* sp., *Cyclotella stelligera*, and *Cyclostephanos dubius* had strong positive primary correlations with chloride concentration while *Synedra ulna* and *Anacystis marina* possessed weaker ones. This anion is independently distributed in the study lakes, and as Hutchinson (1957) and

Drever (1982) have indicated, it is most strongly correlated with either proximity to the world ocean or to ancient sea salt deposits either under the lake or within its watershed. Centric diatoms are more abundant in the world ocean and in brackish inland waters than are the six pennate orders (two of the three centric orders are exclusively marine); consequently, the only question with the first three correlations is what precluded more centric diatoms from correlating with this parameter. While cyanophytes are not abundant in the world ocean, some are quite halide-tolerant (Fogg, et al. 1973); the species name of the cyanophyte which correlated with chloride suggests a similar relationship. Thus, none of these findings are actually new with the exception of the weak one with *S. ulna*. However, these results provide another indirect verification that the selection procedure used here detects "real" relationships.

i. *Stephanodiscus* "*parvus*" in Crater Lake

A small species of *Stephanodiscus* resembling the recently described species, *S. parvus* (Stoermer and Håkansson 1984), was found in both Crater and Squaw Lakes. Whether or not this form was truly *S. parvus*, and not just a peculiar form of *S. hantzschii* was of concern to the botanists who have been studying Crater Lake (C.D. McIntire and R. Truitt 1992 personal communications, E.F. Stoermer 1993 personal communication). While this research can not directly answer whether or not this species is *S. parvus*, it does prove data suggesting that it is not a peculiar form of *S. hantzschii*. When counts of this form are combined with those of *S. hantzschii*, the statistical significance of the correlations for *S. hantzschii* deteriorated. One specific difference observed between these two species was that *S. hantzschii* lacked any relationship with the OrNiCo ratio, while the *S. "parvus"* populations appeared to weakly correlate with it. Thus it appears that this form and the "typical" *S. hantzschii* have significantly different environmental requirements, which supports, but does not prove, the idea that they are different species.

D. Sedimentation Rates and Vertical Changes

Before beginning the discussion of the specific features of interest, a note of caution is necessary; these rates have been maximized by the method of sample site selection. The standard sampling site during this research was the

deepest location in each lake. Wright (1991) has noted that these sites “may have faster rates of sediment accumulation because of resuspension of shallow-water sediments and its deposition in deep water (p. 39).”

1. Todd Lake and a likely eruption of South Sister

South Sister is known to have erupted 2300 years BP., and appears to have also erupted 2050 BP. (Scott 1987). It may have erupted again in the mid 19th century (Orr, et al. 1992, Scott 1990 personal communication). According to Orr, et al. (1992), in 1853 James Miller, a Presbyterian minister, “saw one of the Three Sisters belching forth from its summit dense volumes of smoke (p.160)”; however, a field survey conducted during the 1970s failed to find any evidence of the supposed 19th century eruption (Priest 1990 personal communication). After the field geologists’ failure to find any terrestrial evidence supporting Rev. Miller’s description, they concluded that he (and apparently several other settlers) had misidentified a forest fire (Priest 1990 personal communication), though there was little physical evidence for the latter.

The dated ash fall found in the sediments of Todd Lake during this research provides the first physical evidence that Rev. Miller had observed a minor ash eruption of South Sister in 1853. The seven year difference between the measured and recorded dates (1846 vs. 1853) is not significant because there are several possible causes for an underdate of Todd Lake sediments. The mean sedimentation rate of 0.4 ± 0.1 mm per year means that the physical measurements need to be off by only 2.8 mm for the two dates to exactly match. At least three mechanisms are available to possibly explain the discrepancy. An undermeasurement of the floc layer or the ash particles sinking through that much sediment or some combination of both are two possible explanations for the difference. However, these two mechanisms are not as likely as the third because, first, the original floc measurements have an accuracy of ± 1 mm, and second, the density difference between ash and other particles do not appear to be large as the abiotic particles are clearly separable from the darker material in the varves, thus, significant “sinking” by ash seems unlikely.

The third possible explanation is the change in the degree of sediment compression with depth. Deeper sediments have less water in them and are more compressed than superficial sediments (Håkanson and Jansson 1983). This

phenomenon was also universally observed during this research. The measurements for the mean annual sedimentation rate were all made between 10 and 40 cm as the average rate for the sections being analyzed was of more interest than the vertical variance of the rate. The superficial varves only had to be 3% thicker than those between 10 and 40 cm to completely account for the difference. If the date is corrected by just the difference in the mean percentage of water between 2 and 4 cm vs. that between 5 and 48 cm (94.6% and 92.3%, respectively), the calculated date of eruption becomes 1850, halving the original difference between dates. At this point, further resolution of the data is probably not warranted. There is a second Todd Lake core, collected on 4 September 1986, in storage at the Cascades Volcanic Observatory in Vancouver, WA, and available for future analyses. It is approximately 75 cm in length, so covers a period of time back to about 100 AD., unfortunately ending about 150 years more recently than the next known eruption of South Sister.

2. Anthropogenic Effects on Sedimentation Rates

The sedimentation rates of eight lakes were measured in this study, one directly from varves (Todd), four from pairs of event markers (South Twin, North Twin, Blue and Woahink), and the remaining three from a single change (Oswego) or as an average over the entire history of the lake (Dorena and Walton). The rate of another lake was obtained from the literature (Upper Klamath from Martin and Rice 1981) and that of an tenth (Lake Notasha in the southern Oregon Cascades) was given by Eilers (1992 OLA presentation). With the exception of Bull Run Lake, these are all of the Oregon lakes which have had their rate of sedimentation measured to my knowledge.

The lakes divided into two groups, Oswego and Dorena with rates over one cm per year, and all of the rest with a maximum of only three mm per year. When all eight (North and South Twin Lakes have been treated as being essentially replicates here) with known trophic status index, total dissolved P, chlorophyll *a* concentration and Secchi Disk depth were included in a stepwise multiple linear regression statistical model, none of these factors were significant. However, in the absence of the two high velocity lakes, all of the factors except total dissolved phosphorus had R^2 s over 83%. The best fit was with the chlorophyll *a* concentration (Figure 105, $R^2 = 91.8\%$). These observations fit

Figure 105. Sedimentation rates for seven Oregon lakes vs. chlorophyll *a* concentration (in mg·l⁻¹).

quite well with the hypothesis that lake productivity and sedimentation rates are related, so it was an anticipated finding. The dramatic difference between this relationship and the higher rates found in both Dorena and Oswego appear to require explanation however.

Hecky and McCullough (1984), in studies of the South Indian Reservoir system demonstrated that large new reservoirs tend to have high initial rates of sedimentation. However, even if it is hypothesized that about three-quarters of the total sediments in Dorena were deposited within the first 10 years, this still produces a later sedimentation rate of about 4 mm per year, higher than the much more eutrophic Upper Klamath Lake. Thus, another process is required to explain this rapid rate. Much of the watershed of this reservoir has been logged off (Johnson, et al. 1985). Logging increases the rate of sedimentation (Bormann and Likens 1979, D. Larson 1991 OLA presentation on Mercer Lake). These two processes together, early initial shoreline erosion and sheet erosion due to clear cutting, may adequately explain the high rate.

The cause for the extremely high sedimentation rate in Lake Oswego is entirely anthropogenic. First, the high P inputs from the Tualatin River and over-use of lawn fertilizer causes hypereutrophication in this lake. Second, the addition of copper sulfate to control the blooms produces rapid sedimentation of dead phytoplankters. Thus the large crop of phytoplankton is mostly transported to the sediments. The surviving cells, freed from light limitation, bloom again, and so more copper sulfate is added to remove them. This cycle is repeated every few weeks all season long until either daylength or mixing halts further growth. This appears to be a rather efficient system for producing rapid sedimentation rates.

The second contributing factor to the rapid sedimentation rates in Lake Oswego is that it serves as a settling pond for the abiotic bed load of the Tualatin River. While the relative importance of algal biomass and bed load settling to the high sedimentary rate is unknown; it is clear that the current 50 mm·yr⁻¹ can be expected to fill the 8 m deep anoxic hypolimnion within another 160 years. This will produce a polymictic lake with the only possible limitation on phytoplankton productivity being self-shading.

As indicated earlier, it appears that the water quality of Lake Oswego would be greatly improved if this lake no longer received water from the

Tualatin. Based upon these analyses, if the Tualatin inputs were halted, it seems that the sedimentation rate for this lake would be significantly reduced as well. Such a reduction could produce a clearer, more scenic and enjoyable, lake with a potentially much longer period of use by the local residents and their descendants.

The last lake in this research to demonstrate clear anthropogenic effects is Woahink. Three anthropogenic markers are present, one which is undated. Both of the dated markers are based upon increases in sedimentary vanadium. The first marker is an increase of total V at 10 cm and the second marker is the increase of V relative to Al at 4 cm. The latter is quite probably due to increased automobile travel along Highway 101 after World War II, and gives the 1.0 mm sedimentation rate used above. The increase in total V, but not relative to Al, apparently marks the onset of deforestation in the Woahink watershed, hence an increase in the erosion rate. This change in vegetation cover has not as severe as elsewhere in Oregon, hence the increase in the sedimentation rate is much smaller than for either Dorena or Oswego. If we assume that the increase began about 1860 when the earliest European-American settlers came to the Florence area, then the sedimentation rate during the homesteading period was only about 0.7 mm per year. The rate increase since World War II may be due to an increase in the erosion rate due to more human activity around the lake, or it may be an artifact resulting from a relative lack of compression. The latter possibility, however, can not explain the entire difference in the rate as the percent dry weight is quite stable in the deep station core at between 21.0 and 23.0% from 3 cm down, while the percent dry weight between 0.5 and 3 cm averages 18.2%, or about 83% of that from the deeper sediment depths. Thus the remaining conclusion is that the sedimentation rate in Woahink Lake has increased since World War II, and that a likely cause of this phenomenon is increased human activity in the lake watershed and/or along its shoreline. According to Lewis and Pearl Campbell of the Siuslaw Pioneer Museum (1994 personal communication), lakeshore home building greatly increased during the late 1950s and early 1960s, which supports the observed increase in sedimentation rates of this period.

The undated marker is the sand intrusion with pieces of charcoal in it from the northeastern part of the watershed. The Campbells lack any record of a forest fire in the past 20 years in the northeast part of the Woahink watershed to explain the charcoal. They also report that the Canary Road bridges were replaced in 1974, only 12 years before the 1986 coring, so excluding them as the source of the sand. Thus, the most probable cause for the sand band (and presumably the charcoal as well) is the construction of the state park marina circa 1970.

V. Conclusions

Six significant conclusions were developed as a consequence of this investigation, three general and three specific to individual trace metals.

1. Omernik and Gallant's (1986) ecoregion concept was verified for lake phytoplankton and lacustrine sedimentary diatoms. Although the verification was weak, the ecoregion concept still explained more of the data than did an alternative which approached the information from the perspective of water chemistry and lake productivity.

2. Except under situations of gross heavy metal pollution, trace metals do not seem to alter lake productivity. Instead, their effects are at the species-specific level, determining which species occur and flourish in a particular lake. (Furthermore, even the exception of gross heavy metal pollution does not always hold as the example studied here demonstrated. While copper sulfate additions to Oswego may reduce cyanophyte water blooms, the overall productivity of this lake remained in the hypereutrophic range as documented here by an observed sedimentation rate of 50 mm per year, 17 fold or greater that found in all other lakes measured except Dorena.) The better correlations found between trace metal distribution and ecoregions consequently suggested that trace metal ratios might be part of the cause for the existence of ecoregions.

3. The role of vanadium in controlling the species composition of natural phytoplankton assemblages, as proposed by Patrick (1978, et al. 1975) and Lee (1983), was verified; and their conclusions were extended here to suggest that V pollution from automobile exhaust may be altering species composition, but not productivity, in otherwise unpolluted, or only slightly eutrophified, lakes.

4. High concentrations of filterable nickel appeared to provide a significant competitive advantage to bloom-forming *Anabaenas*.

5. Zinc, required in silicate uptake and mechanism, was demonstrated to be an important limiting nutrient for freshwater diatoms. Data presented here suggest that these organisms have apparently evolved at least three different mechanisms for surviving zinc-deficient conditions.

6. Ratios among these three trace metals as well as Fe, Co, and possibly Mn, in addition to lake productivity indices, provided a number of real world examples which support the resource ratio hypothesis of Petersen (1975),

Tilman (1982), and Sommer (1989, 1993) as a partial explanation for the species richness of lake phytoplankton.

There were several other interesting, but less important, conclusions reached in this research:

7. Of the trace metals other than V, Ni and Zn, Fe appeared to be the most important element and Mo the least. Cobalt was primarily useful as a reference point for measuring the relative significance of other trace metals, much as is aluminum used in aquatic geochemical studies. This investigation suggested, with two exceptions, that further research on the effects of Cu and Mn on species composition of freshwater phytoplankton will probably not be very productive. The exceptions were gross heavy metal pollution and possibly when investigating competition between *Aphanizomenon* and *Anabaena*.

Based upon this research further trace metal studies should probably focus on V, Ni, Zn, and Fe, and possibly include Co and Mn; Cu and Mo do not seem to be important in determining species composition.

8. The discovery here that Todd Lake sediments have annual varves provides geologists and paleoclimatologists with an unusual opportunity for detailed dating of local Oregon geological and climatic events back to at least 2000 yrs BP, and very probably older.

9. The majority of Oregon lakes sampled here, as well as those measured by other scientists, had sedimentation rates of less than 3 mm per year, typically much less. The exceptions, Oswego and Dorena, have been significantly impacted by post-European settlement activities. Otherwise, sedimentation rates in Oregon lakes were primarily associated with lake productivity just as previous research has demonstrated.

10. Vanadium pollution was found in Woahink Lake and possibly minor zinc pollution in both Oswego and Clear Lakes (Marion County).

11. Two forms of metal sulfides were apparently observed in this study. One quickly decomposed when the sediment was aerated through mixing, transforming into an oxide which was subsequently dissolved permanently during the first acid extraction (e.g., zinc sulfide in Squaw Lake); the other was resistant to initial aeration, but decomposed when hot hydrogen peroxide was added to the sediment slurry (examples include East and Todd Lakes). This difference was probably caused by watershed geology.

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VIII. Appendices

Five appendices were assembled as part of this research effort. Only Appendix A, Tables 1 through 7, and Appendix C are presented here. Data in the other appendices are available from the Department of Biology, Portland State University, Portland, OR 97207. Appendix D, Neutron Activation Analyses Results, is also available via the World Wide Web at:

<http://clas.www.pdx.edu/~vogel/tracemetals.html>

All data in these appendices are presented in the following order:

I. Maritime Climatic Regime

A. Coastal Ecoregion

Carter

Eel

Loon

Mercer

Triangle

Woahink

B. Willamette Ecoregion

Clear (Marion Co.)

Oswego

II. Montane Climatic Regime

A. Cascades and Eastern Transition Zone Ecoregions

Big

Blue

Suttle

Crater

East

Paulina

L. of the Woods

Lava

South Twin

Todd

B. Blue and Siskiyou Mountains Ecoregions

Morgan

Walton

Squaw

Appendix A. Fractionated Sedimentary Trace Metals By Depth and Fraction.
1. Mean Iron Concentrations (in μg per g dry weight)

Core Identity	Depth	Exchng.	Organic	Oxides	Available	Residual
Carter #1 (dried)	0	101.	0.00	6940	7045	
	1	5.49	118.	5910	6030	
	2	44.0	18.4	4840	4900	
	5	25.6	0.03	6710	6730	2090
	20	38.6	0.00	3920	3960	
Carter #2	2	24.8	5.49	3800	3840	
	5	16.0	7.04	3070	3100	3050
	20	29.5	13.7	5020	5060	
Carter #3 (St.2)	2	3730	70.7	16700	20500	
	5	2990	71.6	10100	13200	2720
	20	486.	16.3	6070	6580	
Eel #3	2	5760	1160	49400	56300	
	5	7110	674.	45300	53000	6950
	20	6180	587.	37000	43700	
Eel #4	2	5170	606.	54700	60500	
	5	5230	1870	40000	47100	5850
	20	2910	312.	38100	41300	
Loon #3	2	3280	24.3	69700	73000	
	5	3370	16.6	53100	56400	2780
	20	3400	27.9	47800	50600	
Loon #4	2	2350	32.5	45600	48000	
	5	2560	32.4	58700	61300	5120
	20	2540	22.4	59700	62200	
Mercer #3	2	2900	46.4	86200	89100	
	5	5960	364.	34300	40600	9630
	20	6650	101.	55100	61900	
Mercer #4	2	3320	124.	63000	66500	
	5	4550	38.1	52500	57000	8170
	20	5170	30.8	54400	59600	
Triangle #1 (dried)	2	5060	79.7	61200	66300	
	5	6410	173.	69300	75900	2860
	20	5320	9.19	49200	54500	

Triangle #2	2		299.	51800	52100	
(dried, MgCl ₂	5		274.	57300	57600	9440
comb.w/ HCl)	20		126.	49700	49800	
Woahink 89-1	2	1010	56.3	29200	30300	
(St. 2)	5	942.	34.3	18000	19000	5050
	20	830.	8.70	23700	24500	
Woahink 89-2	2	3850	132.	43000	47000	
	5	3810	97.4	41400	45300	7840
	20	3390	74.5	38900	42300	
Clear #1	2	1.72	0.55	415.	417.	
(dried)	5	1.55	0.45	499.	501.	122.
	20	2.29	0.87	389.	393.	
Clear #3	2	305.	126.	36000	36500	
	5	441.	92.0	40000	40500	5910
	20	866.	77.4	36900	37900	
Clear #4	2	230.	11.2	33800	34100	
	5	535.	6.56	30700	31300	10440
	20	238.	17.5	31600	31800	
Oswego #88-1	2	2470	5.83	49700	52100	
	5	1970	12.0	67500	69500	8820
	20	2430	4.51	51800	54300	
Oswego #88-2	2	1320	8.13	46100	47400	
	5	2170	6.91	52700	54900	6750
	20	1550	5.96	58000	59600	
Big #1	2	354.	103.	15200	15600	
(dried, cooked)	5	343.	76.7	8050	8470	22700
	20	240.	35.9	18300	18500	
Big #2	2	732.	92.0	19400	20200	
(cooked)	5	884.	94.3	12800	13800	16200
	20	739.	22.3	11100	11900	
Big #3	2	85.9	13.4	16800	16900	
(St. 2)	5	151.	69.2	16800	17000	30600
(dried, cooked)	20	71.8	7.48	13800	13900	
Big #4	2	543.	24.8	12600	13200	
	5	606.	34.9	11600	12300	9490
	20	596.	17.5	8770	9390	

Big #5	2	235	25.2	17400	17600	11300
	5	354	16.6	15700	16000	
	20	451	47.5	13700	14200	
Blue #4	2	35.3	3.08	5200	5240	4000
	5	38.2	3.07	2700	2740	
	20	74.5	2.65	1230	1300	
Blue #5	2	55.2	0.00	1170	1230	1250
	5	35.1	4.93	976	1020	
	20	49.8	5.61	4700	4760	
Suttle #1 (cooked)	2	92.4	34.4	1190	1310	2270
	5	77.2	22.2	1080	1180	
	20	26.2	23.2	435.	484.	
Suttle #3	2	272.	3.92	1900	2180	2330
	5	344.	7.94	1080	1440	
	20	367.	11.2	542.	920.	
Suttle #4	2	102.	103.	1170	1370	758.
	5	81.2	25.5	1270	1380	
	20	145.	8.84	487.	640.	
Crater #GC1 (South Basin)	2	78.7	11.2	25100	25200	7350
	5	107.	16.2	25400	25500	
	20	295.	5.58	25600	25900	
Crater #88-2 (Wiz. Is. Shlf)	2	74.6	10.5	27100	27100	11600
	5	191.	36.2	25700	25900	
	20	132.	17.7	27900	28100	
East #3	2	47.4	3980	7010	11000	2340
	5	50.1	6330	7650	14000	
	20	101.	4650	6390	11100	
East #4	2	63.7	2200	7190	9450	1430
	5	54.1	2460	5980	8500	
	20	84.7	2720	4600	7400	
Paulina #3	2	102.	247.	104000	104000	1680
	5	69.8	205.	90000	90300	
	20	59.0	16.7	61300	61400	
Paulina #4	2	53.9	137.	73100	73300	901.
	5	46.1	16.0	104000	104000	
	20	82.5	78.1	85400	85500	

L.Woods #1 (dried)	2	171.	7.92	18400	18600	10300
	5	226.	15.3	16900	17200	
	20	1500	3.28	14400	14500	
L.Woods #1R (dried, organic extr. acidified)	2	71.1	9290	7580	16900	10400
	5	69.3	9630	7060	16800	
	20	71.5	12500	7600	20200	
Lava #1 (cooked)	2	158.	27.5	219.	405.	412.
	5	125.	12.5	182.	320.	
	20	205.	46.0	374.	625.	
Lava #2 (cooked)	2	192.	24.8	349.	566.	369.
	5	197.	25.4	270.	492.	
	20	206.	32.6	289.	527.	
S. Twin #3	2	276.	108.	4490	4870	3390
	5	156.	40.3	5130	5320	
	20	141.	17.5	4610	4770	
S. Twin #4	2	205.	83.2	5210	5500	4200
	5	140.	19.2	3210	3370	
	20	231.	55.8	3930	4220	
Todd #3	2	7380	2260	82900	92500	2900
	5	9680	4190	113000	127000	
	20	7860	1930	96700	107000	
Todd #4	2	8430	1410	94800	105000	2430
	5	8470	2930	102000	113000	
	20	7810	2250	93300	103000	
Morgan #1	2	66.8	10.2	23300	23400	3360
	5	117.	13.1	30400	30500	
	20	61.1	7.27	31300	31300	
Morgan #2	2	67.0	7.81	28400	28400	3120
	5	80.4	6.48	36600	36700	
	20	83.4	5.54	29300	29400	
Walton #3	2	50.3	19.1	24900	25000	9100
	5	100.	25.4	14500	14700	
	20	438.	14.7	30200	30600	
Walton #4	2	75.8	13.8	23400	23500	3200
	5	114.	18.9	21700	21800	
	20	335.	22.5	15400	15800	

Squaw #1 (cooked)	2	116.	3.82	90800	90900	4200
	5	137.	5.10	54800	54900	
	20	116.	8.48	60500	60700	
Squaw #2 (cooked)	2	101.	12.3	63900	64000	5140
	5	106.	6.38	67800	67900	
	20	92.1	13.0	61100	61200	

Appendix A. Fractionated Sedimentary Trace Metals By Depth and Fraction.
2. Mean Manganese Concentrations (in μg per g dry weight) :

Core Identity	Depth	Exchange.	Organic	Oxides	Available	Residual
Carter #1 (dried)	0	55.3	3.88	79.0	138.	47.0
	1	5.20	26.0	67.7	98.9	
	2	8.58	6.20	39.9	54.7	
	5	9.18	0.10	63.9	73.2	
	20	2.55	1.99	27.5	32.0	
Carter #2	2	0.91	5.79	29.1	35.8	48.8
	5	0.68	2.59	23.0	26.2	
	20	2.43	3.25	22.5	28.1	
Carter #3 (St.2)	2	149.	23.6	57.3	230.	51.0
	5	115.	3.54	53.1	172.	
	20	26.8	0.44	37.2	64.4	
Eel #3	2	300.	60.4	70.8	431.	40.4
	5	332.	78.2	75.2	486.	
	20	296.	51.0	64.0	411.	
Eel #4	2	258.	48.0	68.5	375.	35.8
	5	281.	54.3	61.6	396.	
	20	218.	41.0	56.0	315.	
Loon #3	2	329.	44.8	225.	598.	15.0
	5	264.	42.4	244.	551.	
	20	229.	55.3	237.	521.	
Loon #4	2	283.	37.7	187.	507.	21.6
	5	427.	105.	223.	756.	
	20	251.	82.3	233.	566.	
Mercer #3	2	457.	80.8	490.	1028.	60.2
	5	300.	111.	124.	535.	
	20	318.	99.0	119.	536.	

Mercer #4	2	410.	79.4	176.	665.	49.0
	5	358.	94.6	148.	601.	
	20	307.	87.3	123.	517.	
Triangle #1 (dried)	2	157.	64.8	229.	450.	27.0
	5	168.	105.	231.	503.	
	20	113.	32.53	179.	324.	
Triangle #2 (dried, MgCl ₂ comb.w/ HCl)	2		75.6	347.	422.	61.7
	5		56.8	342.	399.	
	20		64.9	251.	316.	
Woahink 89-1 (St. 2)	2	324.	96.2	150.	570.	72.7
	5	240.	71.0	82.5	394.	
	20	218.	30.5	106.	355.	
Woahink 89-2	2	404.	136.	138.	678.	80.3
	5	337.	87.5	130.	555.	
	20	381.	82.7	104.	568.	
Clear #1 (dried)	2	172.	30.2	365.	567.	112.
	5	148.	38.2	471.	658.	
	20	119.	39.0	295.	454.	
Clear #3	2	102.1	105.8	201.	408.	85.9
	5	82.8	71.9	238.	392.	
	20	59.0	45.5	238.	343.	
Clear #4	2	77.5	46.9	221.	346.	122.
	5	85.1	63.2	215.	363.	
	20	62.4	61.0	244.	367.	
Oswego #88-1	2	202.	201.	424.	828.	78.8
	5	193.	319.	548.	1059.	
	20	295.	148.	357.	800.	
Oswego #88-2	2	247.	106.	201.	553.	64.9
	5	208.	282.	360.	849.	
	20	196.	242.	401.	839.	
Big #1 (dried, cooked)	2	13.0	10.7	40.1	63.8	357.
	5	9.67	4.88	37.2	51.7	
	20	9.77	3.04	88.5	101.3	
Big #2 (cooked)	2	15.7	3.34	74.9	94.0	193.
	5	16.9	8.91	36.4	62.2	
	20	19.4	11.1	29.7	60.2	

Big #3	2	6.45	0.56	160.	167.	
(St. 2)	5	3.41	1.00	156.	161.	283.
(dried,cooked)	20	6.40	0.14	152.	158.	
Big #4	2	10.8	1.10	39.7	51.6	
	5	14.6	0.00	31.5	46.1	114.
	20	17.7	0.28	31.3	49.2	
Big #5	2	9.92	9.14	43.5	62.5	
	5	16.4	0.26	50.7	67.4	138.
	20	27.2	5.58	35.7	68.5	
Blue #4	2	8.56	2.91	41.0	52.5	
	5	6.16	1.66	22.9	30.7	61.8
	20	9.00	0.45	11.5	20.9	
Blue #5	2	7.53	0.23	9.50	17.3	
	5	7.80	2.39	6.57	16.8	18.5
	20	13.7	2.57	47.9	64.2	
Suttle #1	2	7.84	0.32	8.23	16.4	
(cooked)	5	10.19	0.73	6.31	17.2	34.4
	20	4.98	1.43	2.14	8.55	
Suttle #3	2	16.9	5.58	29.4	51.8	
	5	16.6	3.31	9.87	29.8	34.6
	20	15.9	2.18	6.63	24.7	
Suttle #4	2	7.76	4.41	7.15	19.3	
	5	7.68	3.65	7.17	18.5	14.4
	20	7.37	1.83	3.70	12.9	
Crater #GC1	2	464.	42.6	263.	769.	
(South Basin)	5	453.	60.7	186.	699.	106.
	20	384.	37.6	184.	605.	
Crater #88-2	2	99.9	420.	404.	924.	
(Wiz. Is. Shlf.)	5	288.	52.5	309.	649.	139.
	20	81.3	28.0	227.	336.	
East #3	2	222.	397.	100.4	719.	
	5	364.	415.	92.8	872.	96.6
	20	191.	529.	137.	857.	
East #4	2	204.	356.	69.7	629.	
	5	204.	235.	54.4	493.	57.0
	20	225.	276.	40.4	541.	

Paulina #3	2	874.	2390.	4350.	7610.	79.6
	5	559.	2500.	5370.	8430.	
	20	291.	820.	4000.	5110.	
Paulina #4	2	857.	2440.	2540.	5840.	57.0
	5	654.	1420.	6120.	8200.	
	20	742.	1760.	6370.	8870.	
L.Woods #1 (dried)	2	43.9	11.4	50.4	105.6	70.7
	5	52.6	11.1	31.2	95.0	
	20	55.5	7.78	40.2	103.5	
L.Woods #1R (dried, organic extr acidified)	2	57.6	66.1	15.9	140.	68.6
	5	47.4	49.3	14.9	112.	
	20	49.3	59.4	20.8	130.	
Lava #1 (cooked)	2	6.43	1.21	3.04	10.68	9.54
	5	4.86	2.32	1.82	9.00	
	20	5.16	1.96	0.19	7.31	
Lava #2 (cooked)	2	6.48	12.2	2.00	20.7	7.54
	5	7.43	19.9	2.93	30.3	
	20	7.88	1.18	3.29	12.4	
S. Twin #3	2	43.8	31.9	21.8	97.5	59.8
	5	47.3	13.6	14.3	75.1	
	20	45.5	17.2	15.0	77.6	
S. Twin #4	2	91.8	42.5	21.5	156.	72.9
	5	65.3	15.2	16.4	97.0	
	20	57.7	13.2	14.7	85.6	
Todd #3	2	211.	152.	120.	483.	49.7
	5	187.	256.	221.	664.	
	20	191.	159.	121.	471.	
Todd #4	2	233.	159.	113.	505.	42.2
	5	230.	170.	164.	564.	
	20	236.	127.	123.	485.	
Morgan #1	2	281.	55.0	138.	474.	55.8
	5	211.	42.7	217.	471.	
	20	112.	8.31	176.	297.	
Morgan #2	2	94.1	20.9	176.	291.	51.8
	5	122.	17.1	189.	328.	
	20	62.3	6.32	112.	181.	

Walton #3	2	121.	62.1	139.	322.	84.2
	5	233.	54.4	79.6	367.	
	20	250.	49.8	123.	423.	
Walton #4	2	130.	37.5	119.	286.	51.1
	5	97.4	25.8	94.8	218.	
	20	134.	13.5	56.2	204.	
Squaw #1 (cooked)	2	248.	138.	612.	999.	31.4
	5	159.	15.7	342.	516.	
	20	204.	16.4	323.	543.	
Squaw #2 (cooked)	2	58.1	1540.	1330.	2930.	49.0
	5	38.8	290.	1110.	1440.	
	20	8.27	118.	658.	785.	

Appendix A. Fractionated Sedimentary Trace Metals By Depth and Fraction.
3. Mean Zinc Concentrations (in μg per g dry weight)

Core Identity	Depth	Exchange.	Organic	Oxides	Available	Residual
Carter #1 (dried)	0	CONTM.	0.00	CONTM.		
	1	2.54	1.72	15.1	19.4	
	2	3.30	2.02	16.6	22.0	
	5	1.90	0.65	16.2	18.7	5.20
	20	1.11	0.03	12.7	13.8	
Carter #2	2	0.62	0.06	10.9	11.6	
	5	0.50	0.10	8.07	8.67	10.12
	20	0.53	0.16	10.4	11.1	
Carter #3 (St.2)	2	2.76	1.22	50.4	54.4	
	5	3.42	1.07	27.0	31.5	8.18
	20	1.17	0.45	12.0	13.6	
Eel #3	2	2.57	21.9	69.8	94.2	
	5	0.65	13.5	69.3	83.4	16.4
	20	3.31	17.8	63.7	84.8	
Eel #4	2	2.52	19.0	71.5	93.0	
	5	2.26	30.2	56.8	89.2	12.7
	20	2.33	12.2	54.5	69.1	
Loon #3	2	0.93	0.31	118.	119.	
	5	0.67	0.27	107.	108.	7.53
	20	0.73	0.13	108.	109.	

Loon #4	2	2.34	0.00	109.	111.	11.9
	5	1.66	0.20	107.	109.	
	20	1.37	0.28	105.	107.	
Mercer #3	2	7.24	5.32	100.4	112.9	15.8
	5	2.34	24.1	75.9	102.3	
	20	3.54	14.6	85.8	103.9	
Mercer #4	2	5.36	9.39	89.7	104.4	16.5
	5	3.38	3.18	88.5	95.1	
	20	15.8	31.4	111.8	159.	
Triangle #1 (dried)	2	1.76	1.27	118.	122.	9.74
	5	1.45	2.48	111.	115.	
	20	1.35	0.32	115.	117.	
Triangle #2 (dried, MgCl ₂ comb.w/ HCl	2		6.84	93.0	99.9	28.5
	5		5.88	92.7	98.6	
	20		7.27	85.9	93.2	
Woahink89-1 (St. 2)	2	2.65	1.94	56.1	60.7	16.7
	5	1.75	1.32	32.2	35.3	
	20	2.11	1.55	41.3	45.0	
Woahink89-2	2	1.27	3.76	53.1	58.1	20.7
	5	1.89	3.05	56.9	61.8	
	20	2.01	2.83	54.6	59.4	
Clear #1 (dried)	2	41.7	6.29	180.	228.	28.3
	5	38.7	5.62	219.	263.	
	20	26.9	5.40	125.	157.	
Clear #3	2	0.70	23.5	134.	158.	12.9
	5	1.13	15.6	145.	162.	
	20	1.04	1.66	132.	135.	
Clear #4	2	2.59	3.73	155.	161.	21.0
	5	1.24	6.66	132.	140.	
	20	0.83	1.91	110.	113.	
Oswego 88-1	2	4.07	3.21	189.	196.	20.6
	5	4.37	15.9	197.	218.	
	20	3.29	3.66	144.	151.	
Oswego 88-2	2	9.30	15.2	186.	210.	14.9
	5	2.72	26.1	176.	205.	
	20	1.43	5.2	157.	163.	

Big #1	2	5.78	11.4	58.0	75.1	
(dried,cooked)	5	4.98	8.65	40.4	54.0	46.4
	20	CONTM.	13.16	CONTM.		
Big #2	2	26.0	0.21	78.4	105.	
(cooked)	5	27.7	15.0	54.5	97.3	29.3
	20	CONTM.	114.	127.	241.	
Big #3	2	4.87	0.04	26.1	31.0	
(St. 2)	5	3.00	0.15	25.0	28.2	54.3
(dried,cooked)	20	4.00	0.08	25.9	30.0	
Big #4	2	16.6	5.63	61.1	83.3	
	5	22.2	8.84	64.4	95.4	26.2
	20	39.0	24.4	76.9	140.3	
Big #5	2	20.4	3.82	46.2	70.4	
	5	17.3	0.00	61.0	78.3	15.0
	20	21.1	0.00	48.2	69.3	
Blue #4	2	8.23	1.10	20.6	29.9	
	5	2.68	0.75	12.6	16.0	9.28
	20	3.91	0.00	8.04	12.0	
Blue #5	2	6.66	0.00	7.67	14.3	
	5	6.45	0.78	7.07	14.3	3.31
	20	4.83	0.89	14.9	20.6	
Suttle #1	2	13.0	2.04	27.2	42.3	
(cooked)	5	5.11	0.59	18.49	24.2	11.8
	20	3.70	1.09	5.32	10.1	
Suttle #3	2	20.7	7.20	30.9	58.8	
	5	15.5	1.99	11.3	28.7	7.65
	20	10.9	1.13	7.17	19.2	
Suttle #4	2	6.40	13.0	10.5	30.0	
	5	4.54	7.55	8.42	20.5	5.59
	20	5.64	3.67	4.16	13.5	
Crater #GC1	2	2.32	0.00	47.0	49.3	
(S. Basin)	5	2.53	1.06	55.2	58.8	14.5
	20	1.80	2.36	48.8	53.0	
Crater #88-2	2	1.85	0.24	53.6	55.7	
(Wiz.Is.Shlf).	5	2.58	2.55	58.6	63.7	21.7
	20	2.54	1.84	56.2	60.6	

East #3	2	0.54	16.3	6.75	23.6	7.27
	5	0.54	13.3	6.58	20.4	
	20	0.83	21.5	7.24	29.6	
East #4	2	0.42	13.5	7.29	21.2	4.78
	5	0.61	9.59	5.77	16.0	
	20	0.72	7.54	5.86	14.1	
Paulina #3	2	1.20	1.75	31.2	34.1	4.11
	5	1.07	1.34	28.4	30.8	
	20	0.38	0.38	16.8	17.5	
Paulina #4	2	0.55	1.85	20.8	23.2	2.08
	5	0.71	0.52	16.9	18.1	
	20	1.24	0.66	28.6	30.5	
L.Woods #1 (dried)	2	4.07	3.21	189.	196.	20.6
	5	4.37	15.9	197.	218.	
	20	3.29	3.66	144.	151.	
L.Woods #1R (dried,organic ext. acidified)	2	9.30	15.2	186.	210.	14.9
	5	2.72	26.1	176.	205.	
	20	1.43	5.20	157.	163.	
Lava #1 (cooked)	2	25.3	1.07	3.83	30.2	2.03
	5	28.1	0.05	2.00	30.2	
	20	10.7	0.02	1.52	12.3	
Lava #2 (cooked)	2	CONTM.	1.68	1.87	3.55	0.95
	5	21.5	0.04	0.00	21.6	
	20	9.86	0.00	0.00	9.86	
S. Twin #3	2	11.3	21.1	26.3	58.8	8.46
	5	4.23	7.27	24.5	35.6	
	20	4.84	12.3	40.2	57.3	
S. Twin #4	2	7.42	13.2	13.1	33.7	12.5
	5	4.86	9.02	8.72	22.6	
	20	3.28	10.2	13.9	27.4	
Todd #3	2	1.16	12.7	33.4	47.2	6.29
	5	1.65	18.4	37.6	57.7	
	20	1.71	11.5	39.7	52.9	
Todd #4	2	4.64	17.3	42.4	64.4	5.64
	5	2.66	14.5	33.0	50.1	
	20	2.86	11.1	31.1	45.0	

Morgan #1	2	2.69	1.31	81.2	85.2	9.14
	5	1.38	0.43	88.1	89.9	
	20	1.06	0.49	83.9	85.4	
Morgan #2	2	1.66	0.72	85.5	87.9	7.80
	5	1.76	0.30	86.6	88.7	
	20	0.66	0.42	64.6	65.7	
Walton #3	2	1.72	1.38	83.9	87.0	21.0
	5	1.61	1.58	58.9	62.1	
	20	0.98	0.76	71.4	73.1	
Walton #4	2	1.60	0.81	69.5	71.9	9.89
	5	1.64	0.64	61.3	63.6	
	20	3.78	1.36	54.0	59.2	
Squaw #1 (cooked)	2	2.55	0.43	173.	176.	14.3
	5	1.69	0.24	107.	109.	
	20	1.03	0.60	116.	117.	
Squaw #2 (cooked)	2	3.69	0.59	139.	143.	16.6
	5	4.32	0.13	147.	152.	
	20	1.71	0.22	129.	131.	

Appendix A. Fractionated Sedimentary Trace Metals By Depth and Fraction.
4. Mean Copper Concentrations (in μg per g dry weight)

Core Identity	Depth	Exchange.	Organic	Oxides	Available	Residual
Carter #1 (dried)	0	0.31	0.00	5.17	5.48	1.54
	1	2.10	3.52	8.84	14.5	
	2	0.78	0.37	1.84	2.99	
	5	0.44	0.00	2.31	2.75	
	20	0.30	0.00	2.04	2.34	
Carter #2	2	0.00	0.19	4.14	4.33	7.47
	5	0.00	0.11	3.83	3.94	
	20	0.73	0.65	4.63	6.01	
Carter #3 (St.2)	2	2.18	0.66	10.3	13.2	2.75
	5	2.49	0.65	6.64	9.78	
	20	1.08	0.11	2.15	3.34	
Eel #3	2	0.69	14.5	21.9	37.1	5.63
	5	1.24	13.3	22.3	36.8	
	20	1.67	15.7	18.6	36.0	

Eel #4	2	1.47	14.2	25.7	41.3	6.06
	5	1.34	15.6	18.6	35.5	
	20	2.41	12.3	17.3	32.1	
Loon #3	2	0.46	0.61	38.2	39.2	9.76
	5	0.44	0.61	31.2	32.3	
	20	0.73	0.93	34.3	36.0	
Loon #4	2	0.91	1.09	33.1	35.1	6.20
	5	0.67	1.59	32.4	34.7	
	20	0.92	1.21	34.0	36.2	
Mercer #3	2	1.75	8.72	21.9	32.4	6.66
	5	0.91	12.1	16.1	29.2	
	20	2.06	11.2	20.4	33.7	
Mercer #4	2	1.99	12.4	22.0	36.3	6.99
	5	1.99	6.79	22.3	31.1	
	20	3.27	11.2	20.8	35.3	
Triangle #1 (dried)	2	0.98	3.06	33.4	37.5	3.07
	5	1.33	3.93	27.8	33.1	
	20	1.95	0.79	28.8	31.6	
Triangle #2 (dried, MgCl ₂ comb.w/ HCl)	2		7.18	22.1	29.3	8.70
	5		6.85	21.8	28.7	
	20		6.94	19.9	26.8	
Woahink 89-1 (St. 2)	2	0.20	0.73	10.9	11.9	3.90
	5	0.17	0.38	6.1	6.63	
	20	0.44	1.97	7.5	9.88	
Woahink 89-2	2	0.51	3.69	12.2	16.4	4.32
	5	0.93	1.17	13.1	15.2	
	20	0.96	1.14	12.1	14.2	
Clear #1 (dried)	2	1.91	3.54	43.0	48.4	13.9
	5	2.71	5.46	53.1	61.2	
	20	5.09	5.32	41.1	51.5	
Clear #3	2	0.81	10.00	26.7	37.5	4.43
	5	1.30	4.98	34.1	40.4	
	20	1.83	0.79	36.2	38.9	
Clear #4	2	0.69	4.38	36.4	41.4	7.43
	5	2.07	3.81	33.4	39.3	
	20	1.67	2.18	32.6	36.4	

Oswego #88-1	2	1.20	49.2	252.	303.	7.26
	5	1.84	85.2	277.	364.	
	20	1.27	40.6	190.	232.	
Oswego #88-2	2	1.67	83.4	258.	344.	5.02
	5	1.35	113.	191.	305.	
	20	1.20	45.3	211.	258.	
Big #1 (dried,cooked)	2	1.98	32.7	43.6	78.3	29.7
	5	4.28	25.4	30.9	60.6	
	20	4.88	5.43	89.7	100.0	
Big #2 (cooked)	2	7.53	0.00	70.8	78.3	13.0
	5	9.08	29.0	50.3	88.4	
	20	9.11	32.7	37.9	79.7	
Big #3 (St. 2) (dried,cooked)	2	1.18	0.00	13.1	14.2	37.4
	5	1.18	1.32	14.9	17.4	
	20	1.39	0.00	16.2	17.6	
Big #4	2	0.43	13.8	46.4	60.6	10.3
	5	0.00	14.3	47.1	61.4	
	20	2.49	16.9	43.3	62.7	
Big #5	2	1.90	15.7	42.3	59.9	7.72
	5	3.89	0.00	68.4	72.3	
	20	4.11	25.1	44.0	73.2	
Blue #4	2	3.83	1.95	31.1	36.9	8.26
	5	3.90	1.18	23.4	28.5	
	20	3.34	0.67	17.9	21.9	
Blue #5	2	0.42	1.12	27.4	29.0	5.49
	5	0.56	2.01	19.5	22.0	
	20	1.99	5.05	25.2	32.3	
Suttle #1 (cooked)	2	0.65	0.26	9.55	10.5	6.52
	5	0.00	1.00	11.1	12.1	
	20	0.00	1.93	4.75	6.68	
Suttle #3	2	4.21	8.24	19.5	32.0	7.30
	5	5.41	5.42	16.5	27.3	
	20	5.43	1.97	11.9	19.3	
Suttle #4	2	0.95	9.61	5.44	16.0	2.20
	5	1.03	9.26	6.12	16.4	
	20	3.48	5.11	0.85	9.44	

Crater #GC1 (South Basin)	2	7.03	4.41	55.0	66.4	9.36
	5	11.6	9.55	67.4	88.5	
	20	3.53	7.98	45.4	56.9	
Crater #88-2 (Wiz. Is.Shlf.)	2	5.8	10.1	93.6	110.	15.1
	5	21.9	37.6	70.8	130.	
	20	20.0	26.5	96.2	143.	
East #3	2	0.42	7.79	3.93	12.1	1.51
	5	0.47	6.86	3.66	11.0	
	20	1.25	9.57	3.96	14.8	
East #4	2	1.00	7.48	4.55	13.0	1.45
	5	1.17	6.04	3.42	10.6	
	20	1.65	5.62	3.28	10.6	
Paulina #3	2	0.23	1.18	6.42	7.83	1.30
	5	0.94	1.06	4.63	6.63	
	20	0.88	0.44	9.75	11.1	
Paulina #4	2	2.06	1.11	5.11	8.28	1.26
	5	1.01	0.58	3.31	4.90	
	20	1.13	0.81	5.37	7.31	
L.Woods #1 (dried)	2	2.16	4.22	30.0	36.4	21.3
	5	2.04	5.66	21.6	29.3	
	20	2.27	4.01	28.5	34.8	
L.Woods #1R (dried,organic extr. acidified)	2	0.30	46.2	6.68	53.2	13.4
	5	0.42	29.7	6.86	37.0	
	20	0.53	31.5	9.63	41.6	
Lava #1 (cooked)	2	1.16	1.09	3.53	5.78	2.53
	5	1.27	1.89	2.99	6.15	
	20	1.86	3.47	1.79	7.12	
Lava #2 (cooked)	2	2.96	5.46	1.84	10.26	4.19
	5	3.06	4.42	2.60	10.08	
	20	3.03	3.68	2.07	8.78	
S. Twin #3	2	3.27	19.6	8.67	31.5	4.06
	5	2.27	8.29	6.49	17.0	
	20	2.16	11.8	8.38	22.3	
S. Twin #4	2	3.70	11.8	7.01	22.5	9.55
	5	2.45	6.20	5.70	14.4	
	20	4.63	9.22	4.79	18.6	

Todd #3	2	0.81	9.21	13.5	23.5	4.32
	5	1.53	10.5	11.9	23.9	
	20	1.97	10.2	13.1	25.2	
Todd #4	2	2.60	10.9	11.4	24.9	4.50
	5	2.35	8.78	10.5	21.7	
	20	4.07	8.22	11.8	24.1	
Morgan #1	2	0.50	2.98	33.2	36.7	3.12
	5	0.86	0.98	42.0	43.8	
	20	0.64	0.57	35.0	36.2	
Morgan #2	2	1.13	0.77	39.6	41.5	3.33
	5	1.15	0.57	40.8	42.5	
	20	0.78	0.22	33.1	34.1	
Walton #3	2	0.14	5.72	47.6	53.5	12.2
	5	1.02	4.17	43.4	48.6	
	20	0.72	3.95	49.7	54.3	
Walton #4	2	1.02	2.65	43.4	47.1	4.89
	5	1.02	2.05	38.9	41.9	
	20	1.44	2.19	37.0	40.6	
Squaw #1 (cooked)	2	2.07	1.17	131.	134.	8.42
	5	3.09	0.37	102.	106.	
	20	1.27	0.80	76.6	78.7	
Squaw #2 (cooked)	2	4.45	6.18	112.	123.	4.80
	5	5.61	0.67	131.	137.	
	20	2.00	0.50	96.1	98.6	

Appendix A. Fractionated Sedimentary Trace Metals By Depth and Fraction.
5. Mean Cobalt Concentrations (in μg per g dry weight)

Core Identity	Depth	Exchange.	Organic	Oxides	Available	Residual
Carter #1 (dried)	0	7.63	2.70	5.66	16.0	13.8
	1	0.00	3.06	2.39	5.45	
	2	3.04	1.18	3.41	7.63	
	5	1.73	0.00	2.47	4.20	
	20	2.55	1.00	2.51	6.06	
Carter #2	2	0.49	0.00	2.55	3.04	34.1
	5	0.55	0.19	2.13	2.87	
	20	0.98	0.15	2.67	3.80	

Carter #3 (St.2)	2	9.05	1.56	8.90	19.5	13.5
	5	9.96	0.30	5.17	15.4	
	20	4.46	0.18	2.44	7.08	
Eel #3	2	8.04	10.10	28.3	46.5	26.7
	5	2.60	4.68	26.4	33.7	
	20	6.75	9.49	17.5	33.8	
Eel #4	2	7.83	6.85	15.2	29.8	28.7
	5	3.81	10.10	18.4	32.3	
	20	7.16	6.32	20.2	33.7	
Loon #3	2	3.97	0.24	27.7	31.9	38.9
	5	2.26	0.22	24.1	26.6	
	20	2.47	1.07	24.6	28.2	
Loon #4	2	4.46	0.96	27.2	32.6	43.4
	5	6.81	0.97	24.9	32.7	
	20	6.76	0.97	25.4	33.1	
Mercer #3	2	14.6	8.36	26.7	49.7	45.8
	5	7.40	12.1	13.6	33.1	
	20	13.0	11.6	19.5	44.0	
Mercer #4	2	9.99	7.40	25.4	42.8	33.6
	5	13.6	8.84	24.3	46.8	
	20	20.6	10.5	20.0	51.2	
Triangle #1 (dried)	2	5.59	1.69	26.5	33.8	33.7
	5	6.15	3.36	23.5	33.0	
	20	7.48	1.04	22.1	30.6	
Triangle #2 (dried, MgCl2 comb. w/ HCl)	2		2.06	22.2	24.2	40.7
	5		0.76	14.8	15.5	
	20		1.54	13.5	15.0	
Woahink#89-1 (St. 2)	2	3.22	3.98	15.4	22.6	29.0
	5	2.71	3.13	9.75	15.6	
	20	3.00	2.41	15.0	20.4	
Woahink#89-2	2	5.51	4.88	13.0	23.4	48.8
	5	8.88	5.96	18.1	33.0	
	20	9.42	6.10	24.9	40.4	
Clear #1 (dried)	2	7.92	7.13	22.8	37.8	32.2
	5	8.03	5.11	20.2	33.3	
	20	7.39	3.08	19.1	29.6	

Clear #3	2	4.51	3.08	16.0	23.6	31.1
	5	3.52	2.94	15.7	22.2	
	20	5.15	2.96	20.5	28.6	
Clear #4	2	6.04	3.21	19.0	28.3	36.9
	5	4.32	3.07	20.9	28.3	
	20	2.08	1.93	18.3	22.3	
Oswego #88-1	2	2.65	1.69	21.8	26.2	20.5
	5	6.16	4.49	24.7	35.3	
	20	7.77	3.44	21.2	32.4	
Oswego #88-2	2	4.47	5.50	19.7	29.6	30.7
	5	7.58	8.84	24.4	40.8	
	20	8.00	4.86	25.8	38.6	
Big #1 (dried,cooked)	2	14.3	0.24	26.0	40.5	56.4
	5	14.3	0.00	23.5	37.8	
	20	7.64	0.00	18.5	26.1	
Big #2 (cooked)	2	43.8	6.71	18.2	68.7	10.3
	5	63.7	2.52	17.5	83.7	
	20	50.8	0.03	6.96	57.7	
Big #3 (St. 2) (dried,cooked)	2	8.81	0.83	16.3	26.0	40.3
	5	7.40	0.32	19.4	27.2	
	20	8.14	0.32	17.2	25.7	
Big #4	2	9.23	0.00	16.5	25.7	14.4
	5	19.1	0.00	13.4	32.5	
	20	22.5	0.00	9.64	32.2	
Big #5	2	8.22	5.47	4.98	18.7	23.0
	5	15.4	1.74	5.31	22.5	
	20	24.2	0.00	5.78	29.9	
Blue #4	2	3.10	3.39	0.04	6.53	16.1
	5	3.03	0.00	2.04	5.07	
	20	0.58	0.00	1.47	2.05	
Blue #5	2	1.64	0.00	2.25	3.89	7.74
	5	1.81	0.00	3.20	5.01	
	20	2.17	0.00	2.70	4.87	
Suttle #1 (cooked)	2	17.1	20.6	14.4	52.1	17.1
	5	4.82	12.2	11.8	28.8	
	20	4.41	6.94	3.56	14.9	

Suttle #3	2	17.6	16.4	36.6	70.5	15.1
	5	21.1	3.32	7.26	31.6	
	20	20.4	2.63	15.5	38.6	
Suttle #4	2	5.36	2.02	9.76	17.1	19.3
	5	3.04	3.29	9.24	15.6	
	20	5.67	3.44	8.71	17.8	
Crater #GC1 (South Basin)	2	3.46	4.89	18.5	26.8	19.8
	5	8.21	2.18	19.4	29.8	
	20	8.82	3.46	14.7	27.0	
Crater #88-2 (Wiz. Is.Shlf.)	2	4.29	4.73	20.3	29.3	37.1
	5	7.87	3.33	20.1	31.3	
	20	13.5	6.71	18.4	38.6	
East #3	2	2.96	7.85	5.38	16.2	16.3
	5	2.66	9.94	7.46	20.1	
	20	5.73	7.32	4.82	17.9	
East #4	2	7.27	6.05	1.71	15.0	17.3
	5	6.20	4.59	4.22	15.0	
	20	10.32	4.99	4.49	19.8	
Paulina #3	2	8.26	9.70	46.8	64.8	11.8
	5	6.75	4.73	38.2	49.7	
	20	5.10	2.97	28.5	36.5	
Paulina #4	2	6.43	7.92	38.1	52.5	3.05
	5	6.17	2.15	44.5	52.8	
	20	7.03	2.03	41.4	50.5	
L.Woods #1 (dried)	2	1.05	0.00	13.8	14.8	28.5
	5	4.04	2.18	10.5	16.7	
	20	6.97	1.29	12.8	21.0	
L.Woods #1R (dried, organic extr. acidified)	2	4.45	11.5	6.17	22.1	20.5
	5	2.25	12.6	4.69	19.5	
	20	3.83	13.8	5.73	23.4	
Lava #1 (cooked)	2	12.0	0.00	15.8	27.8	0.00
	5	7.61	2.90	15.8	26.4	
	20	19.7	2.30	0.00	22.0	
Lava #2 (cooked)	2	11.4	4.01	13.4	28.8	0.67
	5	8.33	5.81	1.46	15.6	
	20	11.4	3.72	8.83	23.9	

South Twin #3	2	10.4	2.85	16.0	29.2	14.1
	5	6.10	3.08	9.52	18.7	
	20	3.41	4.49	12.2	20.1	
South Twin #4	2	2.67	7.05	23.8	33.5	6.87
	5	7.73	8.80	11.9	28.4	
	20	10.9	13.3	16.4	40.6	
Todd #3	2	12.0	12.6	11.3	36.0	10.6
	5	15.9	12.3	20.4	48.7	
	20	13.8	10.6	41.5	65.9	
Todd #4	2	12.2	7.15	20.9	40.2	1.70
	5	13.4	9.38	13.0	35.8	
	20	11.0	15.5	10.4	36.9	
Morgan #1	2	5.41	1.79	21.6	28.8	15.9
	5	7.00	2.26	23.7	33.0	
	20	5.74	1.62	134.	142.	
Morgan #2	2	4.26	3.48	18.5	26.2	10.6
	5	5.18	3.53	23.9	32.6	
	20	3.32	1.36	13.5	18.2	
Walton #3	2	1.66	3.63	23.3	28.6	14.5
	5	4.44	6.77	21.0	32.2	
	20	5.18	6.10	18.1	29.4	
Walton #4	2	4.44	4.25	13.9	22.6	21.1
	5	4.27	2.97	15.2	22.4	
	20	4.40	2.16	10.0	16.6	
Squaw #1 (cooked)	2	7.66	2.28	45.4	55.4	39.4
	5	5.47	0.30	31.3	37.1	
	20	6.41	0.50	27.8	34.7	
Squaw #2 (cooked)	2	7.84	3.04	43.0	53.9	42.0
	5	7.46	1.85	47.7	57.0	
	20	7.18	1.16	38.9	47.2	

Appendix A. Fractionated Sedimentary Trace Metals By Depth and Fraction.
6. Mean Nickel Concentrations (in μg per g dry weight).

Core Identity	Depth	Exchange.	Organic	Oxides	Available	Residual
Carter #1 (dried)	0	3.33	0.00	6.69	10.02	
	1	0.00	4.79	0.00	4.79	
	2	1.94	0.75	6.59	9.28	
	5	0.71	0.00	8.52	9.23	7.89
	20	1.46	0.00	6.23	7.69	
Carter #2	2	3.17	0.00	6.05	9.22	
	5	0.34	0.00	5.37	5.71	13.5
	20	3.10	1.50	11.4	16.0	
Carter #3 (St.2)	2	7.16	1.55	13.0	21.7	
	5	7.33	0.65	12.2	20.1	8.12
	20	2.41	0.00	5.92	8.33	
Eel #3	2	7.16	10.5	24.1	41.7	
	5	4.36	11.2	20.0	35.6	21.7
	20	4.46	11.4	26.7	42.5	
Eel #4	2	10.4	9.00	32.2	51.6	
	5	4.90	7.03	21.9	33.8	18.6
	20	5.59	8.95	23.5	38.1	
Loon #3	2	3.37	1.01	57.5	61.8	
	5	1.71	0.58	42.2	44.5	29.9
	20	2.49	0.96	41.1	44.6	
Loon #4	2	4.16	0.20	41.5	45.9	
	5	3.87	1.43	43.2	48.5	24.8
	20	3.32	1.26	42.1	46.6	
Mercer #3	2	5.11	6.95	31.0	43.0	
	5	4.10	15.7	24.3	44.2	23.5
	20	9.64	12.3	29.1	51.1	
Mercer #4	2	7.00	9.88	29.3	46.2	
	5	6.02	11.8	23.3	41.1	22.2
	20	10.6	12.3	24.9	47.8	
Triangle #1 (dried)	2	2.48	1.86	34.8	39.2	
	5	1.88	3.20	32.5	37.6	17.9
	20	5.37	0.92	33.0	39.3	

Triangle #2	2		2.21	25.2	27.4	
(dried, MgCl2	5		4.98	25.5	30.5	38.0
comb.w/ HCl)	20		5.02	27.8	32.8	
Woahink 89-1	2	2.80	2.51	24.9	30.2	
(St. 2)	5	1.84	1.44	15.6	18.9	16.5
	20	2.15	0.91	17.5	20.6	
Woahink 89-2	2	3.45	4.44	19.3	27.2	
	5	6.92	4.35	24.8	36.1	25.6
	20	7.43	6.71	23.3	37.4	
Clear #1	2	10.09	4.21	25.8	40.1	
(dried)	5	9.07	5.27	33.4	47.8	24.3
	20	11.3	2.89	21.6	35.8	
Clear #3	2	0.88	5.48	34.2	40.6	
	5	3.28	4.31	60.3	67.9	17.2
	20	4.43	6.07	37.5	48.0	
Clear #4	2	3.86	3.88	45.0	52.8	
	5	13.0	2.67	33.2	48.9	24.0
	20	4.03	1.54	28.7	34.3	
Oswego #88-1	2	4.14	3.50	31.2	38.8	
	5	7.55	3.34	33.4	44.2	17.7
	20	2.60	2.44	29.0	34.1	
Oswego #88-2	2	7.64	5.31	36.7	49.6	
	5	7.49	5.78	38.6	51.9	18.1
	20	4.60	3.04	36.3	43.9	
Big #1	2	10.2	8.41	31.6	50.2	
(dried,cooked)	5	12.0	10.8	37.2	60.0	40.1
	20	14.4	7.86	34.4	56.6	
Big #2	2	42.0	7.98	41.2	91.2	
(cooked)	5	44.1	9.51	51.4	105.	25.2
	20	31.0	10.05	28.7	69.8	
Big #3	2	30.0	0.29	76.4	107.	
(St. 2)	5	8.17	10.19	51.3	69.7	47.9
(dried,cooked)	20	29.8	1.80	65.4	97.0	
Big #4	2	21.1	12.9	32.9	66.9	
	5	27.3	14.1	37.4	78.8	11.2
	20	27.4	11.2	36.2	74.8	

Big #5	2	15.2	9.54	20.5	45.3	20.8
	5	19.0	6.35	46.9	72.2	
	20	22.4	9.95	33.0	65.4	
Blue #4	2	6.27	3.74	11.8	21.9	10.9
	5	2.91	3.48	6.22	12.6	
	20	4.16	0.42	3.48	8.1	
Blue #5	2	5.05	0.22	2.12	7.39	6.79
	5	2.47	6.37	5.90	14.7	
	20	2.54	4.01	11.1	17.6	
Suttle #1 (cooked)	2	17.9	27.0	30.1	75.0	20.9
	5	8.24	9.36	14.1	31.7	
	20	8.58	13.0	6.66	28.2	
Suttle #3	2	22.4	12.3	26.3	61.0	5.21
	5	16.6	2.32	8.82	27.8	
	20	18.9	2.26	13.9	35.0	
Suttle #4	2	2.57	13.7	5.50	21.8	10.7
	5	3.26	7.39	7.08	17.7	
	20	6.04	7.85	3.39	17.3	
Crater #GC1 (South Basin)	2	4.23	2.67	28.4	35.3	18.8
	5	6.04	3.72	29.4	39.2	
	20	9.14	3.22	25.0	37.4	
Crater #88-2 (Wiz. Is.Shlf.)	2	5.04	3.45	26.3	34.8	25.4
	5	7.51	5.06	29.2	41.7	
	20	8.97	4.63	28.6	42.2	
East #3	2	1.22	4.91	4.44	10.6	6.23
	5	1.23	6.04	2.82	10.1	
	20	3.23	6.26	3.65	13.1	
East #4	2	3.46	4.49	6.33	14.3	6.28
	5	2.35	3.94	5.44	11.7	
	20	11.8	4.70	1.75	18.3	
Paulina #3	2	10.9	33.8	68.2	113.	6.07
	5	7.34	28.4	68.8	105.	
	20	8.18	13.8	50.6	72.6	
Paulina #4	2	14.5	42.5	55.0	112.	1.79
	5	8.11	16.5	109.	134.	
	20	7.75	17.2	69.4	94.3	

L.Woods #1 (dried)	2	15.2	7.26	26.0	48.4	41.7
	5	10.4	3.97	20.1	34.5	
	20	9.46	4.22	29.7	43.4	
L.Woods #1R (dried, organic extr. acidified)	2	4.15	19.7	15.2	39.0	28.3
	5	5.17	20.6	15.4	41.2	
	20	6.02	24.8	19.5	50.3	
Lava #1 (cooked)	2	5.34	0.00	0.00	5.34	0.17
	5	0.26	0.00	0.00	0.26	
	20	2.35	0.00	0.00	2.35	
Lava #2 (cooked)	2	3.79	0.00	0.00	3.79	0.21
	5	6.66	0.00	0.00	6.66	
	20	4.85	0.00	0.00	4.85	
S. Twin #3	2	15.8	30.0	18.3	64.0	6.38
	5	8.67	11.0	25.9	45.6	
	20	10.2	12.8	21.3	44.3	
S. Twin #4	2	21.2	5.38	22.1	48.6	23.4
	5	15.1	13.9	17.6	46.6	
	20	21.3	12.0	25.3	58.6	
Todd #3	2	3.18	7.79	19.2	30.2	10.5
	5	7.91	12.7	16.0	36.6	
	20	15.9	24.1	12.8	52.8	
Todd #4	2	7.76	15.6	11.8	35.1	15.5
	5	3.23	12.0	12.9	28.2	
	20	55.8	43.8	18.6	118.	
Morgan #1	2	3.16	9.21	30.0	42.4	12.6
	5	5.23	2.87	35.0	43.1	
	20	4.67	2.32	89.4	96.3	
Morgan #2	2	2.39	3.21	30.0	35.2	5.38
	5	2.71	2.71	31.5	36.9	
	20	1.78	2.99	25.2	29.9	
Walton #3	2	3.80	6.11	29.7	39.6	18.3
	5	5.10	6.99	24.4	36.5	
	20	3.73	5.38	26.1	35.2	
Walton #4	2	1.97	5.15	20.4	27.5	11.6
	5	2.01	5.23	17.4	24.6	
	20	1.48	3.32	16.6	21.4	

Squaw #1 (cooked)	2	20.5	3.55	226.	250.	41.7
	5	15.8	0.73	290.	306.	
	20	10.3	1.02	163.	174.	
Squaw #2 (cooked)	2	30.5	8.18	316.	355.	41.6
	5	27.3	7.50	353.	388.	
	20	12.1	1.52	299.	313.	

Appendix A. Fractionated Sedimentary Trace Metals By Depth and Fraction.
7. Mean Vanadium Concentrations (in μg per g dry weight)

Core Identity	Depth	Exchange.	Organic	Oxides	Available	Residual
Carter #1 (dried)	0	44.2	9.60	30.9	84.7	0.00
	1	6.71	14.6	14.2	35.5	
	2	4.79	0.00	6.41	11.2	
	5	2.78	0.00	10.9	13.7	
	20	3.75	1.27	7.00	12.0	
Carter #2	2	1.19	2.04	18.4	21.7	12.6
	5	0.00	4.87	16.7	21.5	
	20	1.50	3.39	10.1	15.0	
Carter #3 (St.2)	2	8.90	6.42	56.3	71.6	28.2
	5	11.3	10.16	36.2	57.7	
	20	4.98	2.56	15.6	23.1	
Eel #3	2	27.8	10.2	106.	144.	58.9
	5	22.4	2.99	114.	139.	
	20	7.51	2.34	113.	123.	
Eel #4	2	29.0	10.7	143.	183.	51.4
	5	20.0	19.5	126.	166.	
	20	19.8	13.0	109.	142.	
Loon #3	2	3.42	4.76	140.	148.	45.5
	5	2.85	2.83	115.	121.	
	20	4.45	5.74	134.	144.	
Loon #4	2	6.81	9.70	113.	129.	73.8
	5	9.44	7.70	123.	140.	
	20	5.71	5.20	120.	131.	
Mercer #3	2	19.9	27.8	83.8	132.	73.8
	5	14.4	11.3	83.6	109.	
	20	25.9	18.0	95.8	140.	

Mercer #4	2	34.4	27.4	112.	174.	68.7
	5	49.2	22.9	129.	160.	
	20	34.5	15.4	108.	157.	
Triangle #1 (dried)	2	4.95	4.55	132.	141.	34.8
	5	1.08	3.34	129.	133.	
	20	1.83	1.61	129.	133.	
Triangle #2 (dried, MgCl2 comb. w/ HCl)	2		6.62	119.	125.	58.5
	5		5.51	106.	112.	
	20		7.03	77.3	84.3	
Woahink 89-1 (St. 2)	2	14.2	31.4	53.0	98.6	27.9
	5	7.86	25.1	39.9	72.9	
	20	5.82	7.53	44.3	57.6	
Woahink 89-2	2	13.3	20.4	59.5	93.2	50.2
	5	11.6	25.0	61.6	98.2	
	20	13.9	36.8	38.1	88.8	
Clear #1 (dried)	2	28.5	14.5	141.	184.	70.5
	5	8.05?	38.1	178.	225.	
	20	20.3	11.7	158.	190.	
Clear #3	2	18.9	4.16	127.	150.	32.0
	5	22.7	9.39	109.	141.	
	20	0.34	0.00	113.	113.	
Clear #4	2	5.60	24.6	159.	189.	68.6
	5	18.8	12.4	148.	180.	
	20	11.5	15.2	139.	165.	
Oswego #88-1	2	8.72	5.38	150.	164.	59.4
	5	8.96	6.98	182	198.	
	20	8.24	4.98	144.	157.	
Oswego #88-2	2	11.4	9.71	138.	159.	44.5
	5	10.7	10.6	174.	196.	
	20	7.48	5.24	170.	182.	
Big #1 (dried,cooked)	2	46.3	84.2	47.4	178.	97.6
	5	16.0	84.2	52.9	153.	
	20	40.1	10.1	191.	241.	
Big #2 (cooked)	2	48.0	117.	159.	324.	151.
	5	25.4	83.8	180.	289.	
	20	61.9	94.0	105.	261.	

Big #3	2	0.51	0.00	67.0	67.5	
(St. 2)	5	11.6	16.9	78.5	107.0	165.
(dried,cooked)	20	0.00	0.00	43.6	43.6	
Big #4	2	91.1	154.	215.	460.	
	5	22.8	115.	212.	350.	125.
	20	15.5	96.0	155.	266.	
Big #5	2	47.1	142.	119.	308.	
	5	68.0	22.1	226.	316.	77.8
	20	2.60	121.	206.	329.	
Blue #4	2	17.0	100.	43.0	160.	
	5	21.7	84.2	30.6	137.	24.6
	20	13.4	8.13	49.2	70.8	
Blue #5	2	23.6	15.6	46.2	85.4	
	5	24.0	75.3	15.4	114.7	18.5
	20	0.24	30.2	74.3	104.8	
Suttle #1	2	31.4	46.8	11.2	89.4	
(cooked)	5	12.1	18.2	101.	131.	44.9
	20	3.41	61.0	7.33	71.8	
Suttle #3	2	49.7	111.	58.8	219.	
	5	36.8	94.8	44.6	176.	48.1
	20	29.6	56.1	35.9	122.	
Suttle #4	2	27.4	91.1	46.2	165.	
	5	7.18	70.2	31.4	109.	31.7
	20	3.45	42.7	36.5	82.7	
Crater #GC1	2	22.8	7.77	122.	152.	
(South Basin)	5	15.8	7.68	131.	154.	35.7
	20	6.40	2.31	107.	115.	
Crater #88-2	2	17.9	6.11	114.	138.	
(Wiz.Is.Shlf.)	5	13.6	3.21	116.	133.	71.8
	20	4.89	1.58	115.	122.	
East #3	2	9.87	32.8	42.5	85.2	
	5	17.1	50.6	37.3	105.	8.65
	20	9.12	62.3	31.2	103.	
East #4	2	14.6	22.6	36.9	74.1	
	5	7.5	14.0	43.6	65.1	14.3
	20	17.7	16.2	30.0	63.9	

Paulina #3	2	16.2	43.8	95.1	155.	13.1
	5	21.5	24.7	71.0	117.	
	20	15.0	7.42	55.8	78.2	
Paulina #4	2	63.8	11.2	70.1	145.	6.90
	5	21.4	11.3	81.5	114.	
	20	33.0	17.2	72.4	122.	
L.Woods #1 (dried)	2	6.40	37.4	37.8	81.6	47.0
	5	3.76	30.7	44.5	79.0	
	20	5.90	3.92	81.5	91.3	
L.Woods #1R (dried, organic extr. acidified)	2	7.62	91.9	42.1	142.	42.1
	5	5.43	73.0	33.9	112.	
	20	9.39	86.1	31.8	127.	
Lava #1 (cooked)	2	60.5	125.	50.0	235.	5.61
	5	55.3	72.8	99.5	228.	
	20	62.4	95.2	139.	297.	
Lava #2 (cooked)	2	53.1	106.	25.7	185.	21.6
	5	48.8	122.	11.3	182.	
	20	65.0	96.6	74.5	236.	
S. Twin #3	2	31.6	208.	67.8	307.	20.9
	5	12.5	147.	49.6	209.	
	20	1.93	141.	44.9	187.	
S. Twin #4	2	4.95	145.	188.	338.	27.1
	5	4.86	61.6	88.4	155.	
	20	29.5	120.	205.	355.	
Todd #3	2	37.2	71.3	320.	428.	0.00
	5	52.7	108.	326.	487.	
	20	75.1	97.4	348.	520.	
Todd #4	2	43.2	38.7	309.	391.	0.00
	5	36.2	37.1	307.	381.	
	20	26.4	21.4	366.	413.	
Morgan #1	2	41.0	13.1	107.	161.	50.0
	5	17.2	6.87	133.	157.	
	20	28.5	6.47	149.	184.	
Morgan #2	2	8.15	2.15	127.	137.	34.2
	5	13.2	9.47	142.	165.	
	20	5.73	7.26	104.	117.	

Walton #3	2	29.5	24.1	136.	190.	51.2
	5	67.5	55.8	166.	289.	
	20	27.7	17.2	140.	185.	
Walton #4	2	20.3	18.0	115.	153.	34.0
	5	18.1	16.1	109.	144.	
	20	20.8	15.8	124.	161.	
Squaw #1 (cooked)	2	4.12	5.32	129.	138.	72.9
	5	0.71	1.21	129.	131.	
	20	1.71	2.10	80.9	84.7	
Squaw #2 (cooked)	2	3.07	0.00	131.	134.	138.
	5	5.09	4.58	155.	165.	
	20	2.72	2.99	142.	148.	

Appendix C. Summer Epilimnetic Filterable Molybdate (in nmole per liter)

<u>Lake</u>	<u>nmol MoO₄·l⁻¹</u>	<u>Source *</u>
Carter	5.2	This study
Eel	0.3	Collier (unpublished data)
Loon	0.8	" (" ")
Mercer	1.0	This study
Triangle	1.0	" "
Woahink	0.2	Collier (unpublished data)
Clear	8.3	This study
Oswego	7.3	" "
Big	0.1	Collier (unpublished data)
Blue	2.3	" (" ")
Suttle	1.3	" (" ")
Crater	2.0	" (" ")
East	0.8	" (" ")
Paulina	8.6	" (" ")
L. Woods	1.0	This study
Lava	5.2	" "
S. Twin	5.2	" "
Todd	4.2	" "
Morgan	6.3	" "
Walton	2.1	" "
Squaw	7.3	" "

*: For this study, the detection limit was 1.0 nmoles per liter; Collier's work had a detection of 0.1 nmoles per liter.

All samples from this study were collected between the months of June and September during the years 1985 through 1987 and analyzed in May 1991. The oldest sample was from Lake of the Woods, collected July 1985. Carter, Mercer, and Triangle Lakes were sampled in August 1985.