TRACE METALS IN FRESH WATER PLANKTON

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Abstract

The uptake of Cu, Zn, and Cd by fresh water plankton was studied by analyzing samples of water and plankton from six lakes in southern California. Co, Pb, Mn, Fe, Na, K, Mg, Ca, Sr, Ba, and Al were also determined in the plankton samples. Special precautions were taken during sampling and analysis to avoid metal contamination.

The relation between aqueous metal concentrations and the concentrations of metals in plankton was studied by plotting aqueous and plankton metal concentrations _vs_ time and comparing the plots. No plankton metal plot showed the same changes as its corresponding aqueous metal plot, though long-term trends were similar. Thus, passive sorption did not completely explain plankton metal uptake.

The fractions of Cu, Zn, and Cd in lake water which were associated with plankton were calculated and these fractions were less than 1% in every case.

To see whether or not plankton metal uptake could deplete aqueous metal concentrations by measurable amounts (e.g. 20%) in short periods (e.g. less than six days), three integrated rate equations were used as models of plankton metal sorption. Parameters for the equations were taken from actual field measurements. Measurable reductions in concentration within short times were predicted by all three equations when the concentration factor was greater than 10^5. All Cu concentration factors were less than 10^5.

The role of plankton was regulating metal concentrations considered in the context of a model of trace metal chemistry in lakes.

The model assumes that all particles can be represented by a single solid phase and that the solid phase controls aqueous metal concentrations. A term for the rate of *in situ* production of particulate matter is included and primary productivity was used for this parameter. In San Vicente Reservoir, the test case, the rate of *in situ* production of particulate matter was of the same order of magnitude as the rate of introduction of particulate matter by the influent stream.

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Chapter 1

Introduction

Metal ions are potential toxicants, nutrients, or nuisances in water. Mercury poisoning, or Minamata Bay disease, is an example of the toxic effects of a metal in a natural water system (1). Many metals are essential micronutrients for phytoplankton (2,3) but may be toxic at high concentrations. For example, Cu is essential at low concentrations (3), but is an effective algicide at high concentrations (4). Iron and manganese can impart a metallic taste to drinking water (4) and so are considered potential nuisances. Many industrial processes have unique water quality requirements (5), so metal ion concentrations in water supplies are of concern to industry.

In summary, metal ion concentrations in natural water systems may be important for a variety of reasons. Thus, the processes controlling metal ion concentrations are also important. This thesis is concerned with the role of freshwater plankton in the chemistry of Cu, Zn, and Cd.

Phytoplankton are known to concentrate many metals from water including nutrient and toxic metals (2). That is, the concentration factor, the metal concentration in the algae divided by the aqueous metal concentration, is greater than one. Concentration factors are sometimes greater than 10^5 (This work). Since phytoplankton are the primary producers in most aquatic environments and since they concentrate metals so effectively they have been suspected of participating in the concentration of metals to higher trophic levels in aquatic food webs. However, even the classic example of the concentration of mercury in the marine pelagic food chain from phytoplankton to tuna has been questioned (6).

Whether metals are concentrated in higher trophic levels or not, phytoplankton may serve as an intermediate step in metal cycling. Fowler and co-workers have shown that Cd (7) and Zn (8) are constantly turned over in the body of Meganictyphanes norvegica, a marine filter feeder whose prey includes phytoplankton. They found that the metals were taken up much more rapidly from food than from water. Thus, metals may be concentrated by phytoplankton, eaten by zooplankton, excreted in feces, and sink to the sediments. Small and Fowler state that "M. norvegica can effect a net transport of about 98% of its body zinc concentration below 500 m daily, assuming that no released products are eaten during descent." (8) (Note: This is 500 m deep in the ocean.)

Metal uptake by planktonic algae has been studied in the field and in the laboratory. Laboratory studies have consisted of exposing algal cultures to varying concentrations of metal ions and measuring the uptake. Riley and Roth (9), for example, cultured 15 species of marine phytoplankton and analyzed them for 18 trace metals. They found "... no differences in [the distribution patterns of the metals] which could be correlated with the classification of the organisms." In another experiment they found that trace metal contents of algae generally increased with increasing metal concentrations in the growth media.

Button and Hostetter (10) cultured two freshwater planktonic algae, a diatom and a green alga, and measured Cu sorption and release. They also measured Cu sorption by cleaned cell walls of the two algae. Most of the Cu taken up by the diatom, Cyclotella, was adsorbed on the organic coating surrounding the cell wall or absorbed by the protoplasm. Most of the Cu sorbed by the green alga, Chlamydomonas, was retained by the cell wall. When transferred to a Cu-free medium after Cu incubation, Cyclotella and Chlamydomonas released 46% and 59%, respectively, of the sorbed Cu. This implies that about half of the Cu taken up by these two algae was adsorbed. The Cu concentration in the growth media was not varied.

Conway and Yaguchi (11) varied concentrations of Cd^{2+} and AsO_4^{3-} in continuous cultures of Asterionella formosa, a fresh water diatom. Cadmium sorption "... was found to be a complex function of ambient concentration and time." Desorption of Cd and As was observed in some experiments.

Some field studies have tried to use algae as indicator organisms of metal pollution. For example, Ray and White (12) collected samples of two vascular plants and a blue-green algae, Oscillatoria, upstream and downstream from "base metal" mines. Algae from polluted sites contained much more metal than algae from unpolluted sites. No quantitative conclusions about metal uptake were drawn.

Other field studies have involved measurement of several metals in plankton samples and, occasionally, measurement of metals in both water and plankton. Martin and Knauer (13) determined 18 metals in phytoplankton, zooplankton, and microplankton, a mixture of phytoplankton, zooplankton, and detritus. Their samples were collected in Monterey Bay and on a transect from Monterey, California to Hawaii. Phytoplankton samples were grouped chemically rather than taxonomically. The groups were Ti-containing, Ti-lacking, and Sr-concentrating phytoplankton. Metals in phytoplankton were operationally divided into "organic" and "siliceous" fractions by the dissolution scheme used.

Knauer and Martin (14) measured concentrations of five metals in phytoplankton and sea water from Monterey Bay. They collected their samples at time intervals of three weeks or less over a period of one year. There was a general decrease in the concentrations of Cd, Cu, Zn, and Pb during August 6-13, the period of maximum productivity, but only the Cd decrease could reasonably be accounted for by phytoplankton uptake. All other variations in metal concentrations were attributed to hydrographic effects.

Morris (15) measured dissolved and particulate Zn, Mn, and Cu in Liverpool Bay during a bloom of Phaeocystis, a colonial flagellated alga. A minimum in dissolved Mn occurred at the same time as maxima in particulate Mn and in total flagellate counts. Thus, the decrease in the dissolved Mn concentration was explained by algal uptake. Variations in Cu and Zn could not be explained by algal uptake.

Chau, et al. found that Zn, Zn + Cu, Zn + Fe, and Zn + Fe + Cu concentrations correlated with subsurface chlorophyll a in Lake Erie, but that these correlations were not "highly significant." (16) They did state, though, that "Generally, high chlorophyll a in the western and eastern regions coincided with high concentrations of trace elements."

Holm-Hansen (17) found that small amounts of Cu added to large *in situ* cultures of marine phytoplankton allowed microflagellates to out-compete diatoms. Patrick, Bott, and Larson (18) found that green and blue-green algae were more tolerant of metallic contaminants and that the addition of V, Cr, Ni, Rb, or B to mixed cultures caused population shifts from diatoms to green or blue-green algae. They state that such population shifts " ... may greatly reduce the productivity of the system as a whole. If the shift is to species which have lower predator pressure, large standing crops which may be nuisances may develop."

Mills and Oglesby (19) measured concentrations of Co, Pb, Cu, Zn, Cd, and vitamin B_{12} in Cayuga Lake, New York. They observed that the mean concentrations of all five metals in the euphotic zone decreased as the growing season progressed. They speculated that " ... decreases in the readily available fraction of each trace metal in lake water may [have been] due to a translocation of nutrients in sinking particulate matter during the growing season... or the result of their being incorporated into the metabolic activites of phytoplankton." They also found that the mean concentration of each of the five metals they measured was "among the lowest reported in the literature."

Pita and Hine (20) analyzed Zn, Pb and Cd in reservoir sediments in Oklahoma. They found that Zn and Pb contents of the sediments "closely correlated" with water depth, organic content, and fraction of clay-sized material in the sediments. Based on an assumed rate of sediment accumulation of one inch per year, Fort Gibson Reservoir, Oklahoma, was predicted to remove 0.3 ppm Zn and 0.04 ppm Pb from waters passing through the impoundment.

This thesis describes an experimental project in which plankton and water samples were collected from six southern California lakes while taking special precautions to avoid metal contamination. The water samples were analyzed for Cu, Zn, and Cd and the plankton samples were analyzed for Cu, Zn, Cd, Pb, Co, Fe, Mn, Na, K, Mg, Ca, Sr, Ba, and Al. Special precautions were also taken to avoid contamination during analyses. These precautions are described in Chapter 2.

Copper, Zn, and Cd were chosen for analysis in water because they can be extracted simultaneously from water using APDC + DDDC. (See Chapter 2.) The method has been reported to be useful for Pb, Ag, Ni, and Co as well, but Pb recoveries proved to be unreliable and Ag, Ni, and Co concentrations were so low in the water samples that even after extraction they were not detected. Metal concentrations in the plankton digests were much higher than in water samples, so more metals could be determined.

Other measurements were made to support the measurements of metals in plankton and water and to gain some insight into the role of plankton in metal cycling. Primary production was estimated by measuring oxygen production in light and dark bottles. The flux of sedimenting particulate matter was measured using sediment traps suspended above the lake bottom. The amount of suspended particulate matter in lake water was measured by filtering the lake water through tared filters, lyophilizing the filters, and weighing them.

The data from one of the lakes studied, San Vicente Reservoir, were used in a model of trace metal chemistry in lakes.

The lakes studied were Otay, Morris, Hodges, Castaic, San Vicente, and San Dieguito Reservoirs. All of the lakes are water supply reservoirs. Figure 1.1 shows the locations of the lakes. The main criteria for the choice of lakes were accessibility and distance from the laboratory. The public is not allowed on some of southern California's scarce lakes. Only lakes located within one half day's drive of the laboratory were considered for study.

Otay Reservoir was chosen because it was productive in terms of algal growth and because frequent plankton counts were taken. Hodges and San Dieguito Reservoirs were studied briefly but were dropped because neither lake was particularly productive.

Morris, San Vicente, and Castaic Reservoirs were studied because they were deep lakes with steep sides and relatively small littoral zones. Thus, almost all primary productivity occurred in the pelagic zone and was due to phytoplankton. Hydrologic data were available for San Vicente and Castaic, and plankton counts were also available for San Vicente.

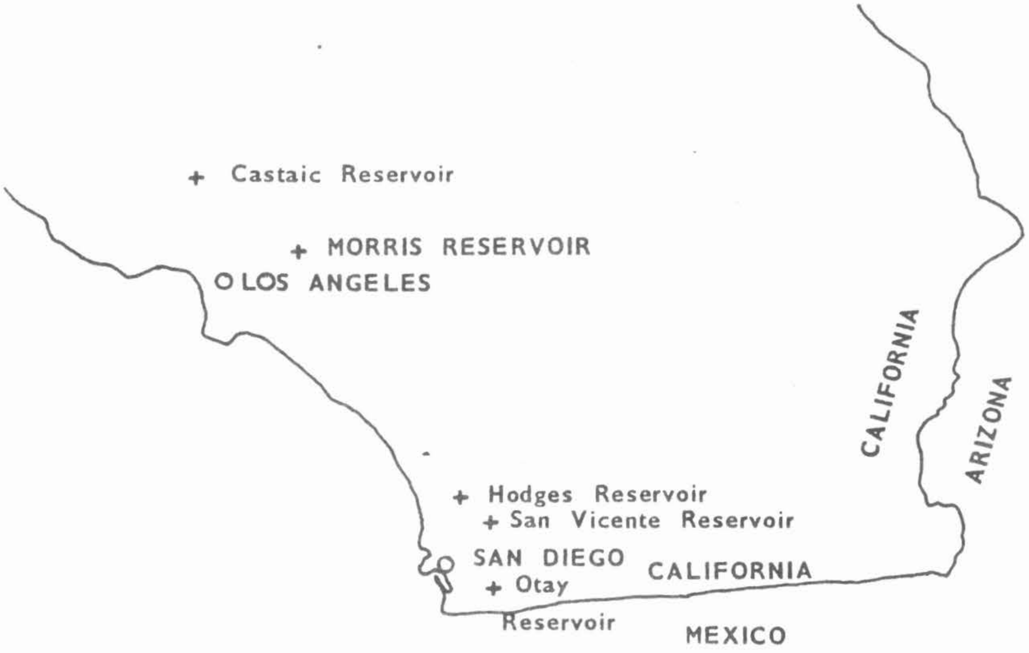

Figure 1.1 Locations of Lakes Sampled.

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Chapter 2

Experimental Methods

2.1 Introduction

This chapter describes experimental methods including cleaning, sampling, and analysis. Cleaning refers to eliminating, or reducing to tolerable levels, metal contamination from sampling gear and labware. Analysis includes sample preparation as well as instrumental analysis.

2.2 Cleaning

Dust from laboratory air, labware, and reagents used in sample preparation are all potential sources of contamination (1). The recommendations of Patterson and Settle (2) strongly influenced all laboratory procedures used in this research.

2.2.1 Cleaning the Laboratory

Access to the laboratory was restricted to those who worked there, usually only the author. Street shoes were left outside and lab shoes, which never left the lab, were worn inside. A lab coat was worn at all times. Non-talced polyethylene gloves were worn whenever labware or samples were handled.

The doors were sealed with rubber gaskets. Polyethylene sheet covered the floor and holes and cracks in the walls. A false wall of polyethylene sheet was put up around the fume hood at one end of the laboratory because it was hard to clean around and under the hood. Ventilation and exhaust ducts had filters which were changed monthly. Counters, shelves, and the floor were periodically wiped with moist tissue to prevent dust buildup.

Brass and galvanized steel fixtures were either removed from the room or, if removal was not feasible, were covered with polyethylene sheet or painted with metal-free paint.

Sample preparation and most cleaning operations were done in a polypropylene laminar flow "clean air bench" with a high-efficiency particulate air (HEPA) filter. The HEPA filter removed 99.97% of all particles larger than 0.3 μm in diameter (3) so that a "class 100" environment was maintained within the bench. Wet ashing was done in a pyrex "oven" which was flushed with filtered N_2. The oven was furnished by Dr. Clair Patterson of the Division of Geological and Planetary Sciences. Heating was done on a hot plate in the fume hood, but the oven was allowed to cool and placed in the clean air bench before opening.

2.2.2 Cleaning Reagents and Solvents

Distilled demineralized water from a pyrex still was used in preliminary rinsing and acid soaking. Water for final rinsing and sample preparation was obtained from Dr. Patterson's laboratory. This water, which will be called Q-water, was distilled in a quartz and Teflon still equipped with an automatic pot dumper and a venturi scrubber to capture particles before they could enter the condenser. Isotope dilution mass spectrometric analysis shows that Q-water has less than 0.1 ng Pb/kg water (7).

Aqueous NH_3 was purified by isopiestic distillation (4). Sub-boiling distillation in an all-Teflon still (5) was used to purify HF, HCl, and HNO_3. Chloroform was washed four times with

HNO_3 to extract metals. Chelating agent solutions, including dithizone (Dz), ammonium pyrrolidinedithiocarbamate (APDC), and diethylammonium diethyldithiocarbamate (DDDC), were purified by exhaustive extraction using purified $CHCl_3$. Buffers were also purified by exhaustive extraction. Double-distilled $HClO_4$, obtained from G. Frederick Smith Chemical Company (GFS), was used without further purification. All purified chemicals except $HClO_4$ were stored in FEP Teflon bottles. The $HClO_4$, which attacks FEP Teflon (4), was left in the borosilicate glass bottle it came in.

2.2.3 Cleaning Labware and Sampling Apparatus

New Teflon and quartz ware was washed with $CHCl_3$ to remove fingerprints and other greasy dirt. It was then dipped in concentrated HNO_3, rinsed, and soaked in 50% (v/v) HNO_3 for at least one day at 60^oC. It was then soaked in warm (60^oC) dilute (0.05%) HNO_3 for at least one day. Finally it was then soaked for at least three more days in fresh warm dilute HNO_3. (Dilute acid is very effective in leaching Pb from plastic surfaces (2), which are probably not smooth on the molecular scale, but porous (7). Dilute acid apparently penetrates the fissures in the plastic surface and dissolves residual pockets of Pb left by the concentrated acid. It was assumed that other metals were leached similarly.) Polyethylene ware was soaked in hot 40% HCl for at least one day and was then treated in the same way as Teflon. Used labware which had been exposed to low metal concentrations was put through the dilute acid cycle before re-use. Otherwise it went through the entire cleaning procedure. Once the cleaning procedure started, equipment was handled only with polyethylene gloved hands or stainless steel tongs held with gloved hands. Final rinsing, transferring, and wrapping were done in the clean air bench.

Nuclepore filters were soaked in 50% HCl for at least one day, then in 0.05% HNO_3 for at least one day, and finally in another 0.05% HNO_3 bath for at least three days. As with all other dilute acid baths for soaking bottles, beakers,... the 0.05% HNO_3 was made fresh from Q-water and GFS redistilled HNO_3. Between acid soaks the filters were thoroughly rinsed with Q-water while held in a plastic filter holder. When cleaning the filter holders they were treated in the same way as polyethylene ware. Polyethylene tubing for the water sampler (section 2.3.1) was cleaned by filling it with hot dilute HNO_3, letting it stand for at least one day, and rinsing with Q-water. This was repeated at least three times before re-use.

Large bottles were stored filled with dilute acid and wrapped in polyethylene film. Teflon separatory funnels were stored in dilute HNO_3 baths. Before an analysis they were filled with a dilute APDC + DDDC solution and allowed to stand for one hour. Small items, such as quartz beakers and transfer pipettes, were either dried in a covered container in an oven and then wrapped with polyethylene film or were used wet from the final acid bath.

Sampling gear was transported to and from sampling sites wrapped in acid-cleaned polyethylene bags.

2.3 Sampling

When sampling from a boat, paint chips and engine exhaust are potential sources of contamination (8). Sampling, therefore, was done from a plastic inflatable raft on all lakes except Morris and Castaic Reservoirs. Private boats are not allowed on Morris Reservoir and inflatable boats are not allowed on Castaic Reservoir, so sampling was done from unpainted fiberglass boats. The boats could not be rowed, so outboard motor contamination was unavoidable. Sampling of water and plankton was done with the boat tied to a buoy with the motor off.

2.3.1 Water Sampling

Water samples from a depth of about three meters were collected using the vacuum apparatus shown in Figure 2.1. In-line filter holders contained Nuclepore filters of 8 μm and 0.4 μm pore size in series. The filter holders were wrapped and kept on ice to minimize microbial degradation of solids before analysis. Unfiltered samples were collected using the sampler without filters.

2.3.2 Plankton Sampling

Microplankton, or net plankton, refers to particulate matter caught by the #25 mesh (64 μm aperture) Nylon plankton net and may, thus, include zooplankton and detritus as well as phytoplankton. Material collected by the plankton net will hereafter be referred to simply as "plankton". Not all plankton samples were examined microscopically due to fear of contamination. Those that were examined appeared to consist mainly of phytoplankton and zooplankton with little detritus. However, the San Diego plankton counts indicated that detritus was a significant component of Otay Reservoir plankton. Details of net construction to avoid metal contamination,

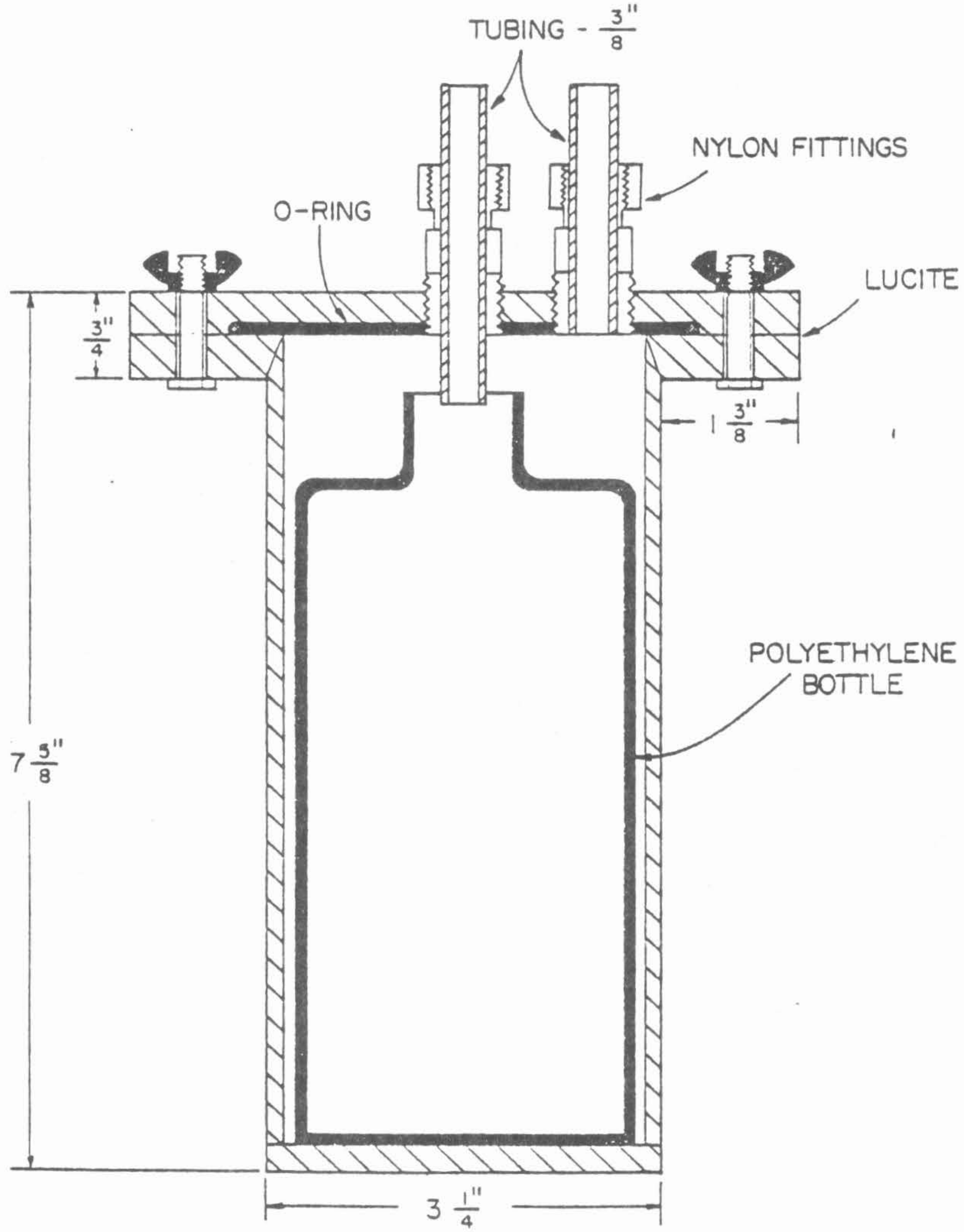

Figure 2.1 Water Sampling Apparatus.

fishing, and sample handling can be found in reference 8. Plankton samples were kept on ice for transportation to the laboratory.

2.3.3 Estimating Gross Photosynthesis

Dark and light BOD bottles were filled with lake water pumped from the depth at which they were to be incubated using the water sampler fitted with a Tygon tube. They were suspended in the lake from early morning until mid-day. Dissolved oxygen (DO) was fixed immediately after incubation by Mn(II) oxidation at high pH (9). The high pH also prevented further biological activity. The azide modification of the classic Winkler Test was used to measure DO (9). The delay between incubation and titration was not more than two days, which is a tolerable delay (10).

2.3.4 Sampling Sedimenting Particles

Figure 2.3.4 shows the design of sediment traps used to measure the flux of sedimenting particles in Morris and San Vicente Reservoirs. Another trap was placed in Castaic Reservoir, fastened to a log boom rather than to a buoy. The line from the log boom broke and the trap was lost. Watanabe and Hyashi (11) found that funnel-type sediment traps collected amounts of sediment in proportion to their areas in quiescent water and that when the areas were extrapolated to zero the collection was zero. Gardner (12) states that this is evidence for 100% trapping efficiency.

2.4 Analysis

Water samples were preserved by acidification to pH 1.6 with purified HNO_3 added to the sample bottle before departure for the

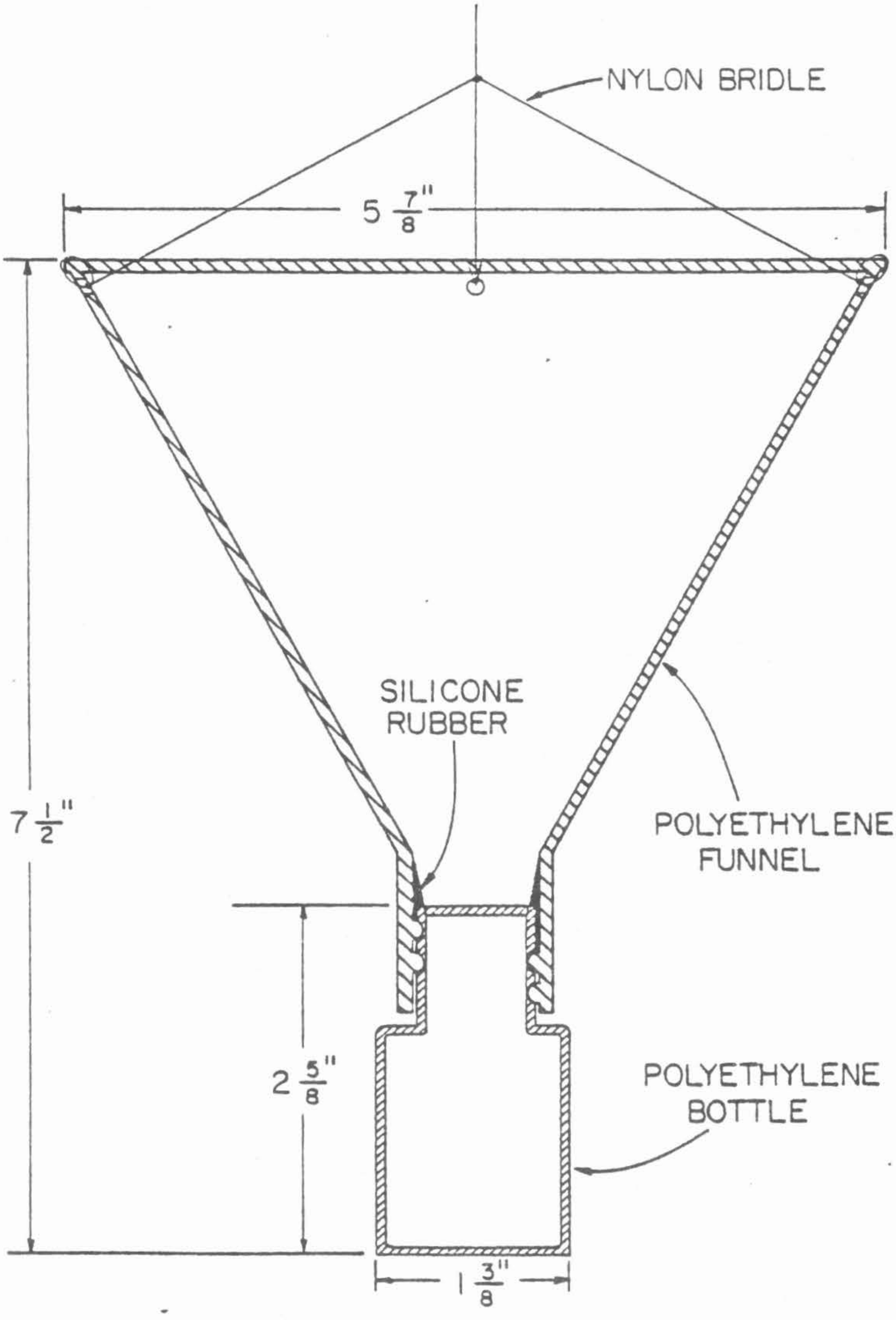

Figure 2.3.5 Sediment Trap.

sampling site. The resulting pH was low enough to prevent growth of organisms and adsorptive losses of metal ions (13). Filters and plankton were kept on ice and in the dark for up to three days, depending on the number of lakes sampled and the distance from the laboratory.

2.4.1 Water Analysis

Filtered samples were heated at least one day at 60°C and unfiltered samples at least four days to insure complete dissolution of metals.

Major cations, Na, K, Ca, and Mg, were determined by atomic absorption spectrophotometry (AAS), aspirating directly into the flame. La(III) was used as a spectroscopic buffer (14).

Chelation by APDC + DDDC (15) and extraction into $CHCl_3$ followed by back-extraction into HNO_3 were used to concentrate Cu, Zn, and Cd for analysis by AAS. Blanks were run in parallel by extracting Q-water. Yields, estimated by spiking samples and extracting in parallel, were greater than 90% for Cu and Cd and greater than 80% for Zn. The yield, which was calculated by comparison with standards, was not checked regularly because standards were extracted from previously extracted sample solutions. Extraction efficiencies were assumed to be constant because a large excess of chelating agent was used, pH was buffered, and identical $CHCl_3$ volumes were used for extraction.

Intercalibration of the extraction procedure was done in cooperation with Dr. Andrew Eaton of the Division of Geological and Planetary Sciences. The results of the intercalibration are listed in Table 2.4.1. Sample numbers refer to sampling sites in San Francisco Bay. The samples were collected by Dr. Eaton. The number of replicates was dictated by the amount of sample available. Agreement was good except for Zn in the "FS" sample for which one replicate analyzed by the author was high.

2.4.2 Solid Sample Analysis: Plankton, Filters, and Sediment

Metal concentrations in freeze-dried solid samples were determined by wet ashing less than one gram of the material in 3 ml of HNO_3 + 1 ml of $HClO_4$. The acids were refluxed at 120°C in quartz beakers covered with quartz watch glasses. When the solution was colorless the watch glasses were removed and the acids were evaporated to dryness. The beakers were then heated at 150°C to drive off $HClO_4$. Residual perchlorates were driven off by twice adding 1 ml of HNO_3, evaporating to dryness, and heating at 150°C to drive off $HClO_4$. Finally, 1 ml of HCl was added to redissolve the metal salts. The acid solutions were rinsed into Tefzel centrifuge tubes, and the solids were separated by centrifugation. The aqueous centrate was defined as the "organic fraction" and was weighed to measure its volume and analyzed by AAS. The solids were defined as the "silica fraction".

The silica fraction was washed with Q-water, dried, weighed, and dissolved in HF. It was then transferred to an FEP Teflon beaker, evaporated to dryness, and heated to drive off HF. HNO_3 was added and evaporated twice to decompose and drive off residual flourides. The residue of metal salts was taken up in 25% HNO_3 and analyzed by AAS.

Table 2.4.1

Results of Intercalibration of Extraction Preconcentration Procedure for Determination of Metals in Solution

	Eaton			Holm		
	9	17	FS	9	17	FS
Cu	2.2	1.37	.37	2.2	1.33	.22
	2.3	1.4		2.2	1.55	
		1.55				
Cd	.16	.16	.088	.15	.12	.081
	.15	.15		.17	.13	
		.18				
Zn	--	--	.52	--	--	.51
						1.02

Notes: 1. Concentrations are in $\mu g\ \ell^{-1}$.

2. Results of replicates listed separately.

3. 9, 17, FS refer to sampling sites.

4. -- indicates data not available for comparison.

Metals in fresh samples were further fractionated by suspending the material in dilute HNO_3 for one hour and centrifuging. The centrate was defined as the "adsorbed fraction" and was weighed and analyzed by AAS. The solids were digested as described in the preceding paragraphs.

The metal fractionation scheme for solid samples was based on the following assumptions: (i) adsorbed metals are held by weak acid adsorption sites on the surface of algal cells, detrital particles, and zooplankton and that dilute HNO_3 (pH 2) can remove these metals but not destroy the organic matter, (ii) organic matter, including cellulose and chitin, is completely destroyed by HNO_3 + $HClO_4$ digestion and, therefore, that this digestion dissolves all metals in cell walls and cytoplasm, and (iii) HNO_3 + $HClO_4$ does not dissolve silica, but HF does. Aluminosilicate minerals, such as clays, would be included in the silica fraction if they were present in a plankton sample. Si:Al ratios in the plankton samples analyzed in this work suggest, though, that clays were not serious contaminants. All acids used in this fractionation scheme were purified by sub-boiling distillation. (See Section 2.2.2).

Segar and Gilio (16) found that major cations interfered seriously with the determination of trace metals in marine organisms analyzed by wet ashing and flameless AAS. They extracted their digests with APDC to remove the interfering ions. In plankton digests in this work major cations were sometimes a nuisance, but not a serious hindrance. That is, total Na + K + Mg + Ca concentrations were less than 0.05 M. Rather than extract the digests, standard matrices containing Na, K, Mg, and Ca chlorides in the molar ratio of 1:1:1:5, which was a rough average of the first few plankton samples, and closely approximating the total major ion concentration were used to match sample matrices for Cd, Pb, Co, and Cu determinations by flameless AAS. Major ion interferences were apparently not serious in flame AAS.

The method was tested by analyzing orchard leaves, NBS Standard Reference Material 1571. Results for Cd, Zn, Pb, and Cu, the only metals analyzed, were within the range of values reported by NBS. Blanks were determined in parallel digestions using empty beakers for plankton and sediment blanks and clean filters for filter blanks.

One plankton sample, San Dieguito 6/23, was analyzed by Michael Burnett of the Division of Geological and Planetary Sciences using isotope dilution-mass spectrometry. He determined that the Pb, Ca, Sr, and Ba contents were 0.24, 4.860, 62.5, and 405 g g^{-1} dry weight, respectively. (Plankton results appear in Table 3.3.1.)

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Chapter 3

Results

3.1 Introduction

Results of metal measurements in water and plankton are presented in this chapter. Concentration units are in μg l^{-1} for water, rather than moles l^{-1}, in order to be consistent with plankton metal measurements. Plankton metal concentrations are expressed in units of μg g^{-1}. Some water concentrations have been translated to moles l^{-1}.

3.2 Metals in Water

Table 3.2.1 lists metal concentrations in the waters of the lakes sampled. For the Castaic samples S1 refers to a sampling site near the inlet while S2 is a site near the dam. The San Vicente samples are labeled I and L which stand for inlet and lake, respectively. The San Vicente lake sample was collected near the dam. A bar indicates an unacceptable result. For example, if a metal concentration in a filtered sample was significantly higher than in the unfiltered sample (relative average deviation or RAD > 20%), the former was assumed to be erroneous.

Parentheses indicate suspect filtered concentrations. If a filtered concentration was higher than the unfiltered concentration but the RAD was < 20%, the error may have been due to very low metal content in the suspended particles and variances in analytical results.

Some metal concentrations in filtered samples were higher than in the corresponding unfiltered samples and contamination

Table 3.2.1

Metal Concentrations[1] in Filtered and Unfiltered Lake Waters

Lake	date[2] sampled	filt. f unf. u	Concentrations					
			Cu		Zn		Cd	
			µg ℓ$^{-1}$	nM	µg ℓ$^{-1}$	nM	µg ℓ$^{-1}$	nM
Otay	3/22	u	2.15		--[3]		.063	.6
	6/4	u	1.07		--		.002	
	6/23	u	1.31		ND[4]		.005	
		f	1.30		--		.0093	
	7/6	u	2.45	39.	ND		.0057	
		f	.79		--		--	
	8/26	u	1.86		.36		.0055	
		f	--		--		--	
	12/1	u	1.70		3.0		.0092	
		f	1.37		2.4	37.	--	
Morris	6/8	u	.98		--		.0031	
	6/28	u	.61		ND		ND	
		f	--		--		--	
	8/20	u	.53	8.	.15		.0075	
		f	(.57)[5]		.15		.0020	
	11/17	u	.60		.54		.0049	
		f	.58		.15		.0019	.02
	12/17	u	.87		.66		.020	
		f	.60		--		.014	
Castaic S1[6]	1/10	u	1.72		.37		.03	
		f	1.59		.073	1.	.03	
	1/24	u	1.02		.76		.0117	.1
		f	.98		.40		.0074	
Castaic S2[6]	1/10	u	1.45		[7]		.0226	
	1/24	u	.74		.73		.0126	
		f	.64		ND		ND	

Table 3.2.1 (Continued)
Metal Concentrations[1] in Filtered and Unfiltered Lake Waters

Lake	data[2] sampled	filt. f unf. u	Cu		Zn		Cd	
			$\mu g\ \ell^{-1}$	nM	$\mu g\ \ell^{-1}$	nM	$\mu g\ \ell^{-1}$	nM
San Vicente I	1/19	u	4.82	76.	1.43		.0033	
		f	4.78		.61		.0017	.02
	1/26	u	.74		1.09		.0126	
		f	.64		.87		ND	
San Vicente L	1/19	u	4.54				ND	
		f	4.51		.69		ND	
	1/26	u	.49	8.	1.11		.0030	
		f	.49		1.04		.0021	
Hodges	6/5	u	2.42		1.77		.031	
	6/22	u	1.62		2.06		.026	.2
		f	(1.83)		--		.0083	
	7/7	u	2.96		.48		.0011	
	8/25	u	1.45		.74		.005	
		f	--		--		--	

Table 3.2.1 (Continued)

Notes

1. Most concentrations are in μg ℓ^{-1}. Some are translated to nM.
2. Sampling period was from March, 1976 to January, 1977.
3. -- indicates unacceptable result. See text.
4. ND indicates metal was not detected by AAS.
5. ( ) indicates suspect result. See text.
6. See text for explanations of S1, S2, L, I.
7. Blank indicates missing data.

during filtration was believed to be the explanation. The problem first appeared in the 7/7 and 8/25 samples. (The 7/7 samples were analyzed after the 8/25 sampling trip.) The filter holders were found to be the source of contamination, as was shown by filtering Q-water through the water sampling apparatus with and without filter holders. The filter holders were cleaned using the same procedure for sampling trips before 7/7 and there was no contamination problem then. Before 8/25 filters were discarded. After 8/25 the filters were digested like plankton except there was no silica fraction. That is, there was no visible residue after HNO_3 + $HClO_4$ digestion. The filtered concentration was then defined as unfiltered concentration minus filterable concentration.

3.2.1 State of Metals in Suspended Particles

Table 3.2.2 lists concentrations of metals in two states, "adsorbed" and "organic", and in two size classes of particles, those removed by an 8μ Nuclepore filter and those passing the 8μ filter but retained by a 0.4μ filter. The adsorbed fraction is operationally defined as metal removed by suspending the filter in 0.05% HNO_3, pH 2, centrifuging, and decanting. The organic fraction is operationally defined as metal obtained by digesting the "desorbed" filter in HNO_3 + $HClO_4$. No visible solid remained after digestion and evaporation,so there was no refractory or "silica" fraction.

The Castaic S1 1/24, San Vicente L 1/26, and San Vicente I 1/26 filters were not desorbed, so the organic fraction and adsorbed fraction were combined.

Table 3.2.2

Particulate Metal Concentrations[1] in Lake Waters: Size Class and Fraction

	Lake:[2]	Morris	Morris	Otay	Castaic S1	Castaic S2	San Vicente I	San Vicente L	San Vicente I	San Vicente L
	Date:[3]	11/17	12/17	12/1	1/24	1/24	1/19	1/19	1/26	1/26
Metal	Fraction[4,5]									
Cu	.4 A	ND	.078	ND	*[6]	.03	.031	.011	*	*
	.4 0	.364	.059	.025	.0223	.01	.0033	ND	ND	ND
	8 A	.573	.073	ND	*	.046	ND	.021	*	*
	8 0	1.05	.059	.181	.0225	.01	.0052	ND	ND	ND
Cd	.4 A	ND	.0017	.0017	*	.01	ND	ND	*	*
	.4 0	.0019	.0026	.0085	.0009	ND	.0039	.0015	.0014	.0009
	8 A	ND	ND	ND	*	.012	ND	ND	*	*
	8 0	.0025	.0018	.0065	.0034	ND	ND	.0011	.0016	ND
Zn	.4 A	ND	ND	.242	*	.29	.026	.12	*	*
	.4 0	.163	.14	.287	.205	.12	.044	.031	.21	.01
	8 A	ND	ND	ND	*	.42	.068	.092	*	*
	8 0	.204	.26	.545	.157	.09	.024	.035	.01	.06
Fe	.4 A	1.17	2.7	2.31	*	1.8	ND	.38	*	**[7]
	.4 0	21.8	17.0	40.3	47.3	28.7	12.4	6.35	33.4	**
	8 A	2.25	6.9	4.95	*	1.8	.25	.58	*	**
	8 0	61.8	41.3	122.	43.	20.4	4.55	6.90	12.	**
Mn	.4 A	2.14	1.8		*	1.8	1.22	.30	*	*
	.4 0	2.16	1.35	25.1	.66	.74	.40	.50	2.14	.22
	8 A	4.76	5.17	ND	*	2.3	1.26	1.57	*	*
	8 0	3.78	14.5	27.8	.60	.64	1.01	1.17	.55	.9

Table 3.2.2 (Continued)

Notes

1. Concentrations are in $\mu g\ \ell^{-1}$, i.e. μg of particulate metal in a given size class and chemical fraction in one liter.
2. See section 3.2 for explanation of the symbols S1, S2, I, and L.
3. Sampling period was 3/76 to 1/77.
4. 8 indicates metals caught by 8μ Nuclepore filter .4 indicates metals passing 8μ filter and caught by 0.4μ filter.
5. A stands for adsorbed fraction
   0 stands for organic fraction
   See text for explanation
6. Castaic S1 1/24, San Vicente I 1/26, and San Vicente L 1/26 filters were not desorbed, so 0 is actually A + 0.
7. Fe data are missing for San Vicente 1/26 L filters.

3.3 Metals in Plankton

The concentrations of fourteen metals in plankton expressed in units of $\mu g\ g^{-1}$ (dry weight) are listed in Table 3.3.1. Two fractions, organic and silica, were operationally defined for all but four plankton samples. The organic fraction was obtained by digesting freeze-dried plankton in $HNO_3 + HClO_4$, corresponding to adsorbed plus organic fractions. The silica fraction was obtained by dissolving in HF whatever solids survived the digestion.

A bar indicates that the measurement was not made. This was usually because there was no sample left. (Flame AAS consumes sample solution.) Mn was not measured in the Otay 6/5 sample, though, because Mn absorbance was so high that it was off-scale and the sample was discarded before it could be diluted and measured. Blanks were unusually high (i.e. about 20% of signal) for Cu, Zn, and Fe in the San Vicente plankton. These metal values are in parentheses.

3.4 Metals in Sedimenting Particles

Table 3.4.1 lists the fluxes of sedimenting particles trapped by the particle interceptors placed in Morris and San Vicente Reservoirs. Table 3.4.2 lists the metal contents in the combined adsorbed and organic fractions of the particles.[1] The San Vicente sample was too small to spare part of it for moisture determination.

---

[1] The silica fractions were accidentally discarded by someone who shared the author's laboratory.

Table 3.3.1

Metal Concentrations[1] in Fresh Water Plankton

Sample[2] Metal:	Cd	Pb	Co	Cu	Zn	Mn	Fe	Na	K	Mg	Ca	Sr	Ba	Al
Otay, 6/5														
A + 0	.0497	.0312	.21	2.9	21.1	--[3]	142	4390	8340	2660	14000	--	--	79.4
S	.00887	.0262	ND	.175	.297	3.80	16.7	--	--	--	--	--	--	113
Otay, 6/24														
A + 0	.071	.20	.45	20.3	65.7	646.	558.	2620	9620	1280	11970	--	--	--
S	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Otay, 7/6														
A + 0	.0718	1.08	.644	21.7	149.	797.	1180	2240	9300	1600	17400	331	500	512
S	.00595	ND	.142	1.77	ND	152	70.9	--	39	101	390	8.35	--	375
Otay, 8/26														
A + 0	.158	ND	.575	5.69	15.6	296	294	4490	12900	3230	10900	--	--	47
S	.0156	ND	ND	5.61	5.20	57.2	--	--	--	--	--	--	--	346
Otay, 12/1														
A	.995	5.55	7.92	12.8	116	926	206	16500	47200	6960	16800	2250	1390	ND
0	.185	3.78	1.72	30.4	17	53	3820	3600	2000	4640	10300	169	ND	21300
S	.0043	.284	.320	.520	.500	5.47	236	--	--	--	--	--	--	2140
Morris, 6/28														
A + 0	ND	ND	ND	ND	2.08	191	148	646	1140	661	3250	--	--	120
S	ND	.0249	ND	.166	.282	23.6	--	--	--	--	--	ND	ND	120
Morris, 9/20														
A + 0	.0336	20.1	.635	47.2	64.7	490	2530	1250	964	1370	14700	274	441	1350
S	.00529	.195	.202	2.63	8.02	135	226	--	183	150	222	19.8	--	1120
Morris, 11/17														
A	5.57	1.98	10.8	10.3	53.9	450	360	3830	7390	1660	2750	153.	191	221
0	ND	.113	1.43	15.2	28.7	73	5020	200	1410	270	730	17	ND	5470
S	.284	.588	.181	.310	.568	5.36	325	--	--	--	--	34.5	60.3	2490

Table 3.3.1 (Continued)

Sample	Metal: Cd	Pb	Co	Cu	Zn	Mn	Fe	Na	K	Mg	Ca	Sr	Ba	Al
Morris, 12/17														
A	1.37	5.11	4.45	2.63	33.0	600	389	1040	2530	709	5230	48.2	ND	58
0	1.34	.938	.764	.850	43.2	790	3420	1550	7570	1650	2580	11.7	924	1550
S	.0144	--	.347	.366	4.43	32	399	1160	968	182	417	--	348	4980
San Vicente, 1/19														
A	.915	1.66	6.70	7.90	110	198	52.9	1300	5160	728	2090	191	ND	--
0	.115	.189	.26	1.67	33	178	542	1880	4760	672	1070	110	79.3	556
S	ND	ND	ND	(.063)	(.013)	1.77	(8.7)	24.5	23.4	20.2	3.99	ND	ND	108
Hodges, 7/7														
A + 0	.134	.503	.478	14.6	34	205	644	4400	8450	1100	2660	63.4	112	561
S	.0018	.00702	ND	.426	1.01	8.18	5	--	5.36	3.62	543	ND	--	25.3
Hodges, 8/25														
A + 0	.204	.374	.528	15.3	37.1	144	1420	920	3810	1030	3100	71	193	1290
S	ND	ND	.078	.457	1.65	38.9	97.5	--	51	31	76.2	51	--	455
San Dieguito, 6/23														
A + 0	.0221	.346	.207	18.4	--	51.9	167	220	823	232	351	34.5	278	184
S	ND	.0274	ND	.223	ND	3.96	4.38	--	11	3.96	4.49	5.19	--	109

Notes: 1. Concentrations are in $\mu g\ g^{-1}$ (dry wt.).

2. A adsorbed fraction, 0 organic fraction, S SiO_2 fraction (definitions in text).
A + 0 adsorbed plus organic fractions, dilute HNO_3 treatment omitted.

3. -- indicates measurement not made (see text).

Table 3.4.1

Flux of Sedimenting Particles in Morris and San Vicente Reservoirs

Lake	Date[1]	Area $(cm)^2$	Collection Period (days)	Amount Collected (g)	Flux $(g\ cm^{-2}\ day^{-1})$
Morris	7/15	206	30	2.4 (d)[2]	3.9×10^{-4}
Morris	11/17	206	43	22.5 (f)[3]	2.5×10^{-3}
San Vicente	1/26	366	7	1.04 (f)	4.1×10^{-4}

Notes:
1. Date collector was retrieved.
2. Dry weight.
3. Fresh weight.

Table 3.4.2

Metal Concentrations in the Organic Fraction of Sedimenting Particles[1]

Lake: Date Collected: Metal	dry wt.[2] Morris 7/15	wet wt.[2] Morris 11/17/76	wet wt.[2] San Vicente 1/26/77
Cd	.617	.164	.0917
Pb	7.66	.808	.242
Co	7.12	1.27	.903
Cu	29.3	32.5	6.38
Zn	165.	60.2	12.0
Mn	1680.	1410.	1300.
Fe	26200.	26200.	6350.
Na	438.	56.5	41.7
K	6430.	7640.	1240.
Mg	13410.	11800.	2010.
Ca	111000.	12800.	1790.
Sr	1180.	263.	78.0
Ba	ND	1460.	264.
Al	17100.	4460.	2970.

Notes: 1. Concentrations are in $\mu g\ g^{-1}$.

2. Only Morris 7/15 sediment was freeze dried.

Chapter 4

Discussion

4.1 Introduction

This chapter discusses the data presented in Chapter 3. Plankton metal contents have been plotted as a function of time and the plots have been compared with one another and with similar plots of aqueous metal concentrations vs time. The fraction of total Cd, Zn, and Cu associated with plankton in unfiltered water was calculated from plankton counts and plankton metal contents. The rate of uptake of metals by plankton is discussed. A model of trace metal chemistry which includes a term for in situ particle formation is considered.

4.2 Patterns of Plankton Metal Contents

This section will attempt to relate aqueous metal concentrations to plankton metal contents. It is assumed that plankton sorb uncomplexed or "free" metal ions from solution. For example, equilibrium computations have shown that growth rate correlated strongly with free Cu^{2+} concentrations in cultures of marine phytoplankton (13).

To see whether comparison of aqueous and plankton metal concentrations is meaningful, the speciation of Cu, Zn, and Cd in lake water was computed using the equilibrium program MINEQL (14). Since this was a "worst case" computation (i.e. the smallest fraction of free Cu, Zn, or Cd), the Cu, Zn, and Cd concentrations used were the highest measured. Alkalinity, pH, and Ca, Mg, Na, and K concentrations were measured while concentrations of ligands other than OH^- and CO_3^{2-} that are representative of fresh waters were assumed (15). The humic and proteinaceous material of natural organic matter was modeled by salicylic acid, phthalic acid, and glycine. Details of the computation are in the appendix.

Essentially all of the Cd and Zn was computed to be free or complexed with inorganic ligands, so variations in organic ligand concentrations would not have affected Cd or Zn speciation appreciably. Since pH varied by no more than 0.1 pH unit and alkalinity varied by less than 5% in any lake, Zn and Cd were always at least 96% and 89% uncomplexed, respectively. Thus, comparing total aqueous Zn and Cd concentrations with plankton Zn and Cd concentrations is meaningful.

Speciation of Cu was more complicated with only 3% of the total Cu computed to be uncomplexed. Some of the Cu was computed to be bound by salicylate and glycinate. Thus, variations in natural organic ligand concentrations could result in variations in free Cu^{2+} concentrations. Thus, relating aqueous Cu concentrations to plankton Cu concentrations is not straightforward if only free Cu^{2+} is sorbed.

Changes in metal concentrations in plankton and water were compared. Matching water and plankton patterns were expected to indicate passive sorption. Langmuir and Freundlich plots were also attempted with no apparent correlation.

Figure 4.2.3 shows plots of Cu, Zn, and Cd concentrations in unfiltered water vs time for Otay Reservoir and Figure 4.2.4 is a similar plot for Morris Reservoir. Concentrations in unfiltered

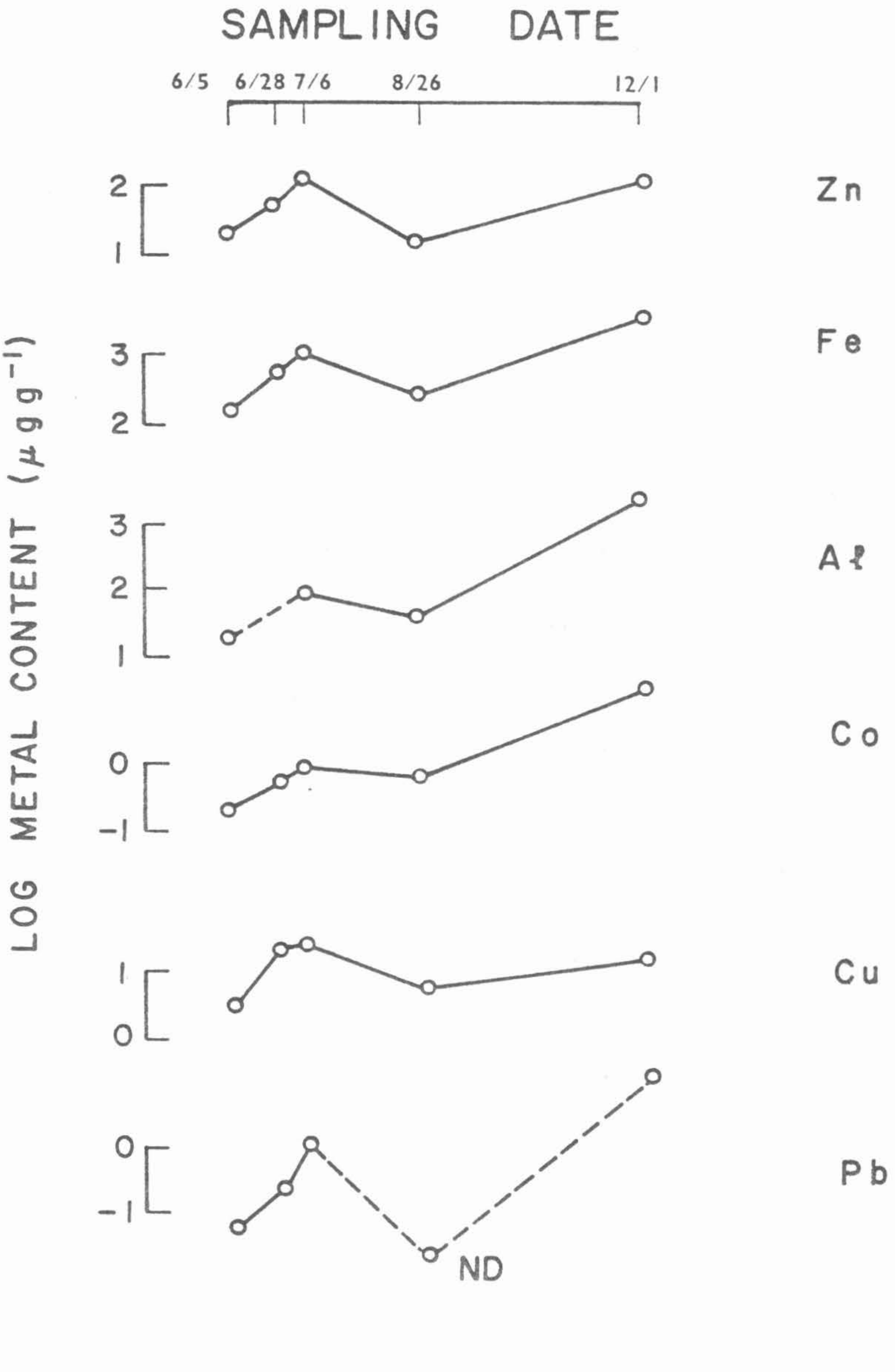


Figure 4.2.1 Otay Plankton Metal Contents Plotted

vs Sampling Date.

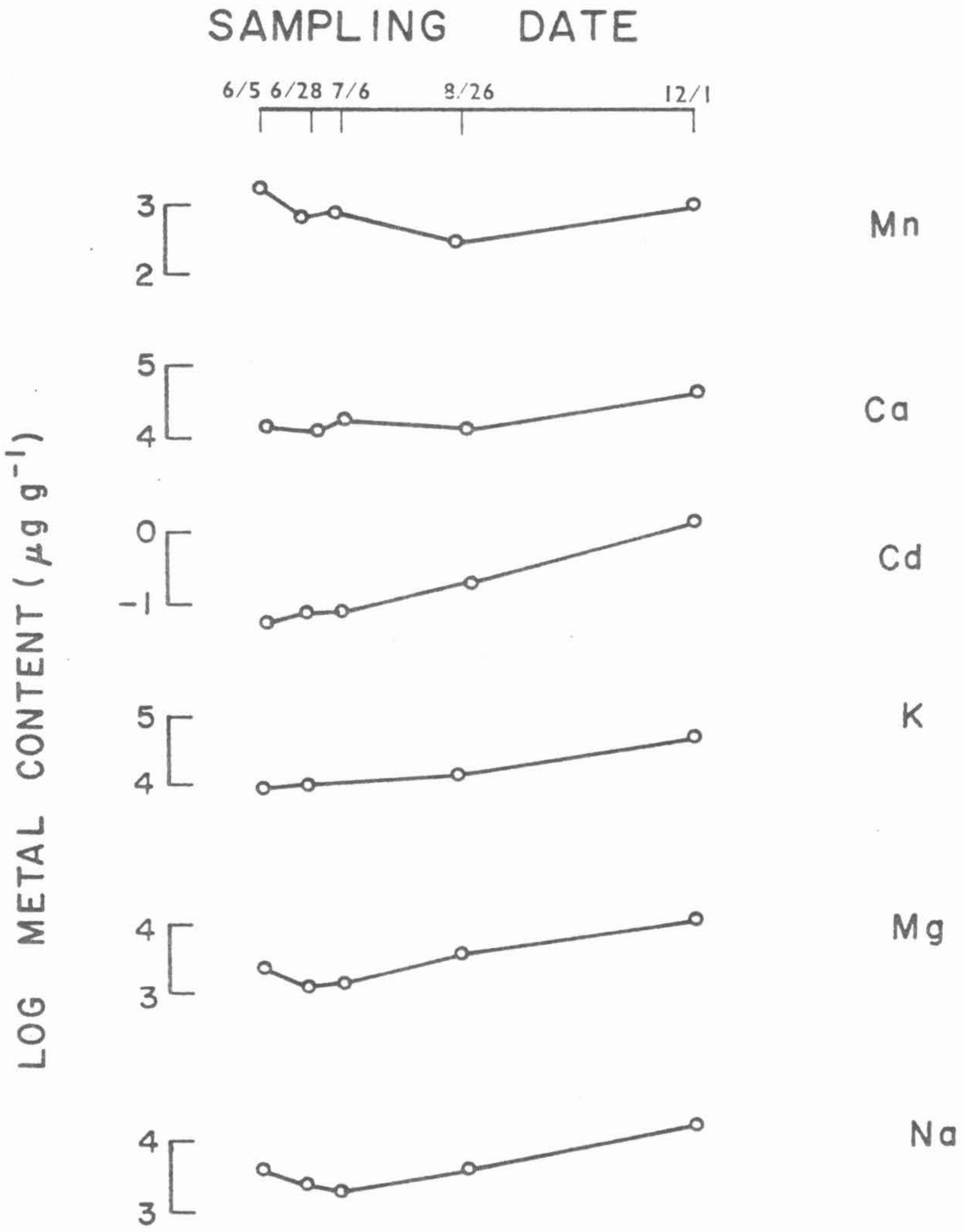


Figure 4.2.1 (Continued)

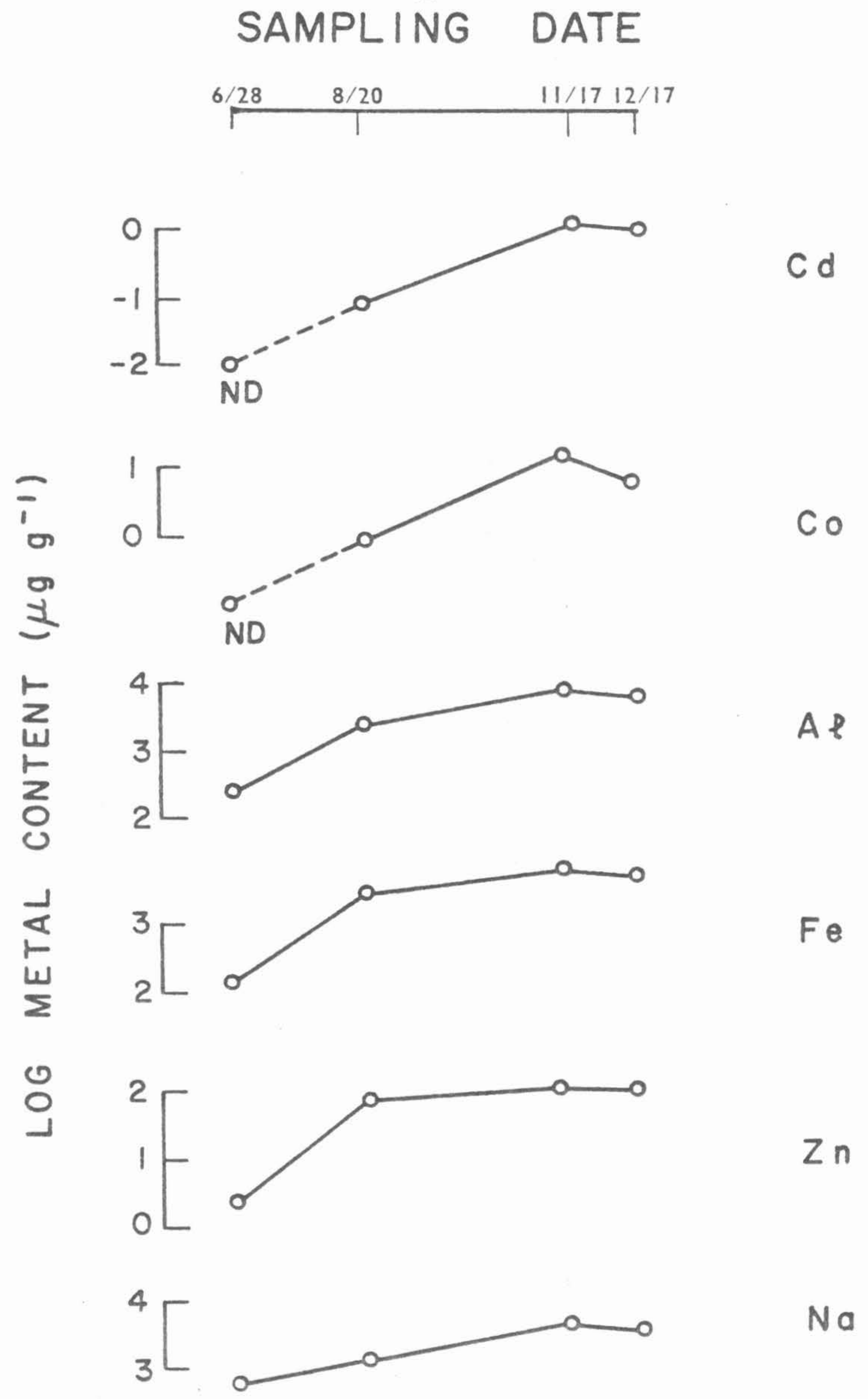


Figure 4.2.2 Morris Plankton Metal Contents Plotted

vs Sampling Date.

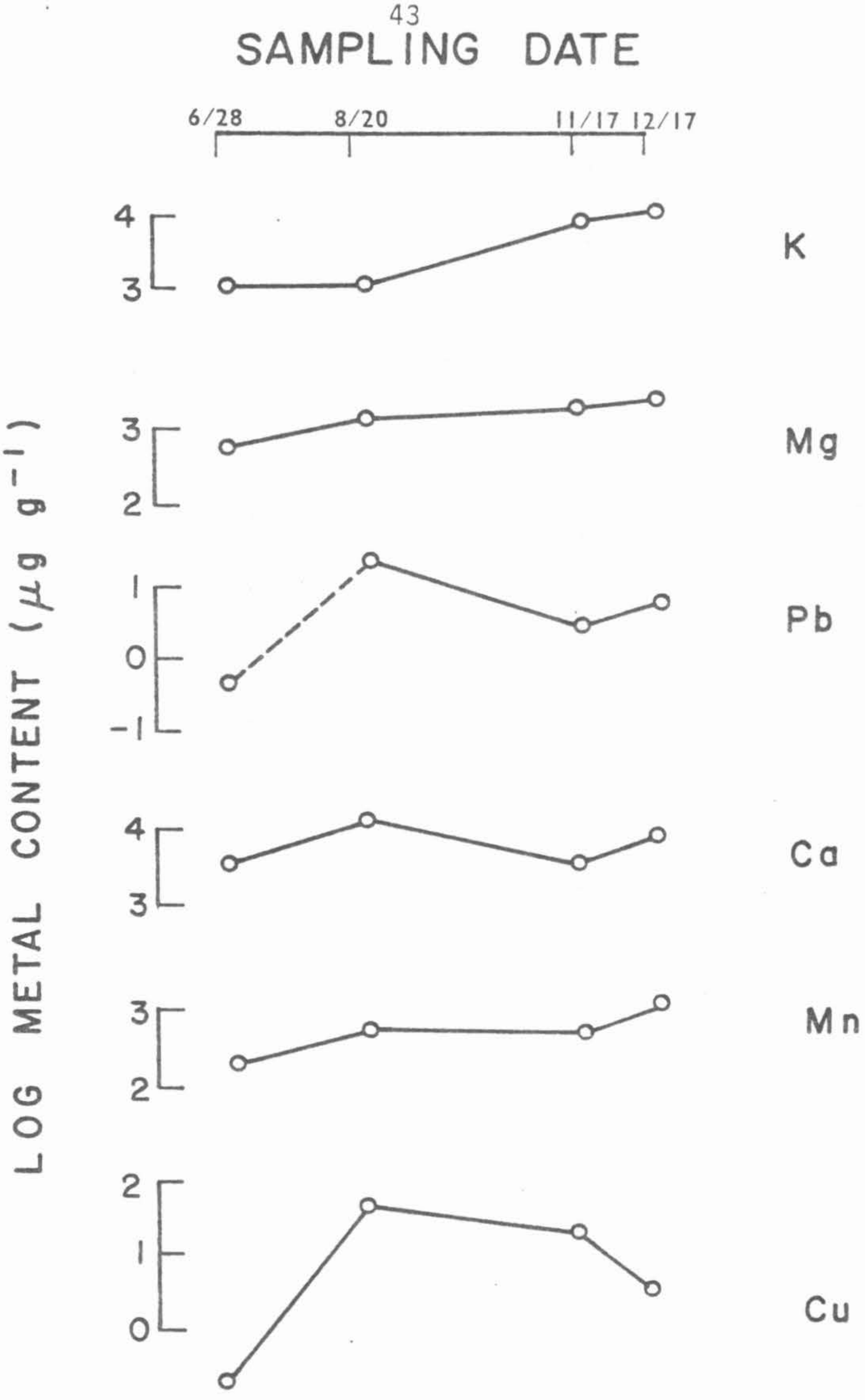


Figure 4.2.2 (Continued).

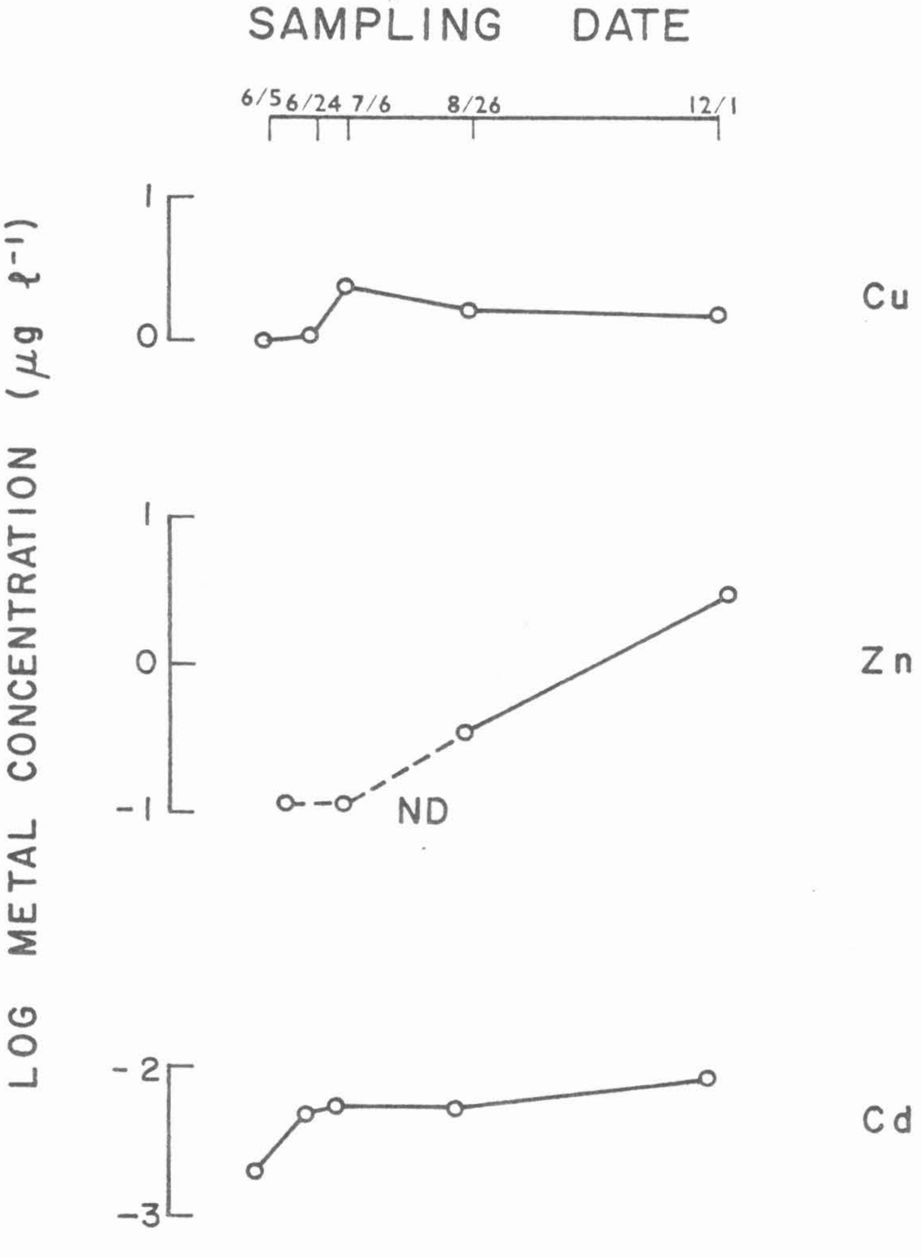


Figure 4.2.3 Metal Concentrations in Water from Otay Reservoir Plotted vs Sampling Date.

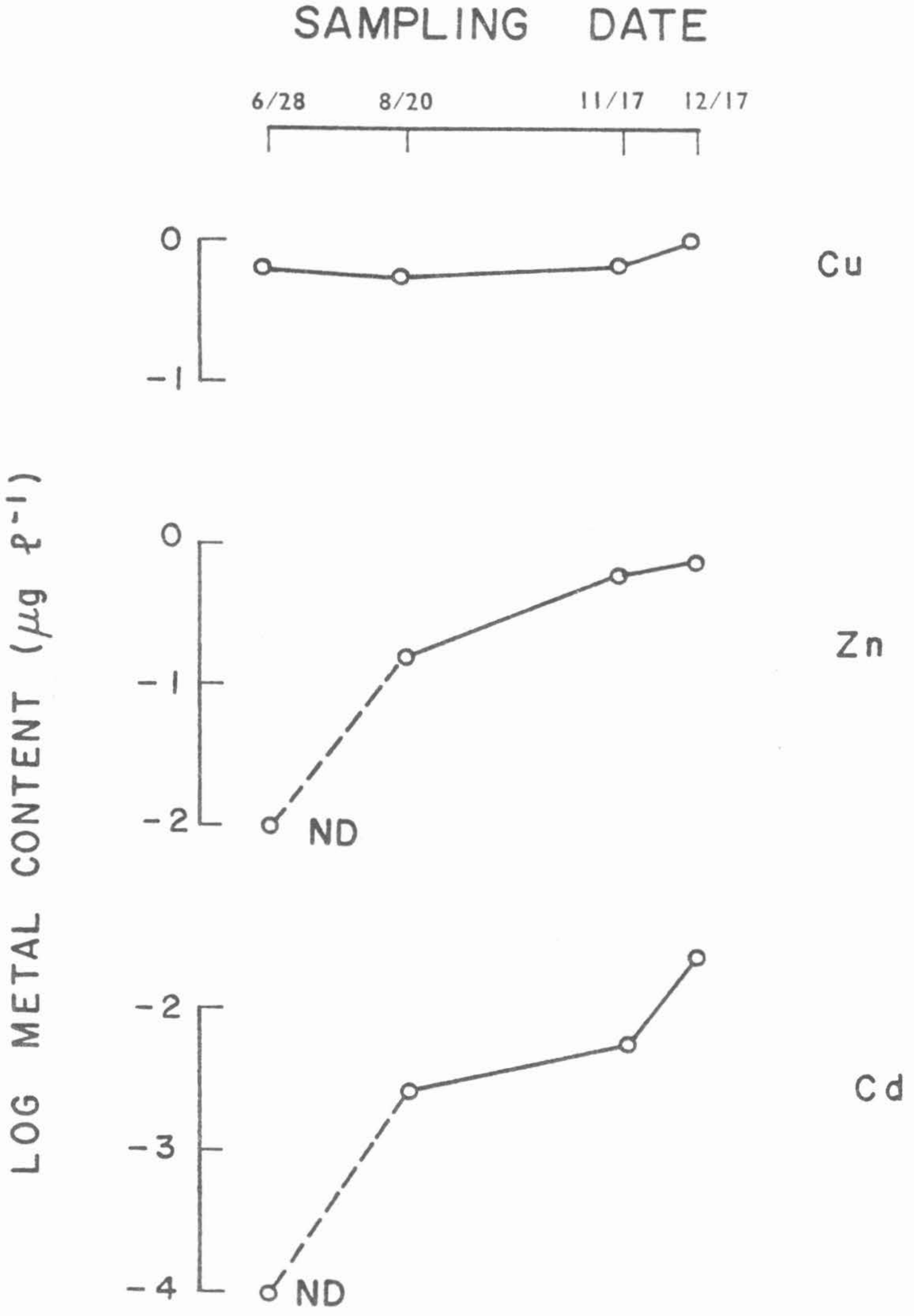


Figure 4.2.4 Metal Concentrations in Water from Morris Reservoir Plotted vs Sampling Date.

Table 4.2.1

Trends in Otay Plankton and Water Metal Concentrations

Metals	Trends[1]								
	6/5		6/24		7/6		8/26		12/1
plankton									
Zn, Fe, Al, Pb		+		+		-		+	
Ca, K		0		0		0		+	
Cd, Na		0		0		+		+	
Co		+		+		0		+	
Mg		-		0		+		+	
Mn		-		0		-		+	
Cu		+		0		-		+	
water									
Cu		0		+		-		0	
Zn		*[2]		0		+		+	
Cd		+		0		0		+	

Notes: 1. + increase
0 little change
- decrease

2. no Zn in water data

Table 4.2.2

Trends in Morris Plankton and Water Metal Concentrations

Metals				Trends			
	6/28		8/20		11/17		12/17
plankton							
Cd, Co, Al, Na		+		+		0	
Zn, Fe, Mg		+		0		0	
Pb, Ca		+		-		+	
Mn		+		0		+	
K		0		+		0	
Cu		+		-		-	
water							
Cu		0		0		+	
Zn		+		+		0	
Cd		+		+		+	

Notes: 1. + increase > x2

0 little change

- decrease < ÷ 2

water were used rather than in filtered water because some filtered water concentrations were unacceptable. Comparison of Figures 4.2.3 and 4.2.1 and of Figures 4.2.4 and 4.2.2 should show whether plankton metal concentrations reflected changes in aqueous metal concentrations. If the ability of plankton to concentrate metals remained constant despite species changes, metal contents in plankton should reflect trends in aqueous metal concentrations, if not the magnitude of such trends.

The trends in Cd plankton and water concentrations in Otay Reservoir were similar and the magnitudes of the overall changes from 6/5 to 12/1 were nearly equal. Thus Cd uptake by Otay plankton between June and December, 1976, may have been governed by aqueous Cd concentrations. The June to December trends in plankton and water Cu were similar, though short-term changes were different. Cu uptake by plankton may also have reflected aqueous concentrations. The Zn water and plankton plots were dissimilar between 6/5 and 8/26 and similar in direction, if not magnitude, from 8/26 to 12/1. Plankton Zn uptake may have been independent of aqueous Zn concentration before 8/26 and dependent on aqueous Zn concentrations after 8/26.

On comparing the concentration patterns of Cu, Zn, and Cd in water and plankton from Morris Reservoir (Table 4.2.2) it appears that Morris plankton Cu contents did not reflect aqueous concentrations. Changes were opposite in sign and plankton Cu content changes were greater in magnitude. Plankton and water patterns were somewhat similar for Zn in that there were large increases between 6/28 and

8/20 and little or no increase between 11/17 and 12/17, but the plankton Zn concentration remained practically constant from 8/20 to 11/17 while the water concentration doubled. The water and plankton patterns for Cd were similar from 6/28 to 11/17. Then the plankton Cd concentration remained constant until 12/17 while the aqueous concentration doubled. Aqueous Cd and Zn concentrations may govern plankton Cd and Zn contents in Morris Reservoir.

Cadmium uptake by both Otay and Morris plankton seemed to reflect trends in aqueous Cd concentrations. The uptake of Zn by Morris plankton may have been governed by aqueous Zn concentrations, but Cu uptake did not seem to reflect trends in the aqueous Cu concentrations. The opposite can be said about Otay plankton. Cu uptake may have been governed by aqueous Cu concentrations but Zn uptake probably was not governed by aqueous Zn concentrations. Plankton counts from Morris Reservoir were not available for the period sampled, so comparison with Otay counts to see if the species compositions were different was not possible.

Metal contents of Otay plankton are plotted as a function of time in Figure 4.2.1. Figure 4.2.2 is a similar plot for Morris plankton. The lines connecting the points in each graph are not meant to imply continuous changes in metal contents with time but merely to make any patterns easier to see. Dotted lines signify that an intermediate data point could not be plotted due to missing data (i.e. Al in Otay plankton collected 6/24) or concentratins which were too low to detect. Points representing samples whose concentrations were too low to detect are marked "ND".

The metal contents in the series of plankton samples from either lake were compared with one another to see if there were similarities between plots or "patterns". Two or more patterns were considered similar if the series of changes in metal contents between sampling dates were identical. The criteria for changes were as follows:

1. Increase: metal content increased by at least a factor of two.
2. Decrease: metal content decreased by at least a factor of two.
3. Little Change: metal content neither increased nor decreased according to criteria 1 and 2.

The trends in metal contents of Otay plankton are listed in Table 4.2.1 along with trends in Cu, Zn, and Cd concentrations in unfiltered water. Table 4.2.2 lists the corresponding trends in Morris plankton and water.

Three patterns of changes in metal content in Otay plankton were common to two or more metals. Zn, Pb, Fe, and Al all followed the same content pattern. Ca and K followed another pattern and Cd and Na followed a third. The remaining four metal content patterns did not resemble other patterns.

Morris plankton metal contents also had three patterns which were followed by two or more metals. One group included Cd, Co, Al, and Na. Another group included Zn, Fe, and Mg. The other group was Pb and Ca. The remaining three metals followed different patterns.

These similarities of patterns suggest that plankton metal contents are due to chemical properties of plankton and not to random fluctuations. Twenty seven patterns can be formed by four points *that satisfy* the criteria mentioned above. Thus, for Morris Reservoir there were 2.25 times as many possible patterns as metals, yet three patterns were followed by groups of two to four metals. The similarities between the Otay plots are even more striking because five points can form 81 possible patterns.

4.3 The Fraction of Metal in Lake Water Associated with Plankton

Some plankton may not have been captured by the plankton nets used in this study, since some of the species known to be present are small enough to fit through the 64 μm apertures of the Nylon mesh. On the other hand, the net was not used as a strainer. It is generally assumed that the plankton organisms roll down the side of the net to the container in the cod end as the net moves through the water (1). Whether or not all species were captured by the net, it was assumed in the following calculations that the metal contents of net plankton were the average contents of all plankton.

Plankton counts for Otay Reservoir were obtained from the San Diego Water Utilities Department and appear in the Appendix. Plankton distributions in lakes may be non-uniform or patchy (16) so the San Diego plankton counts may not estimate plankton biomass with more than order of magnitude accuracy. However, the fractions of metals calculated to be associated with plankton were so small that accuracy in estimated plankton biomass was not important. The counts were expressed as standard units ml^{-1}. Standard units ml^{-1} can be converted to $\mu m^2\ ml^{-1}$ by dividing by 4.25 (2). The areas were converted to volumes using the information on algal cell geometry shown in Table 4.3.1 (3,4). Some information on cell

Table 4.3.1

Cell Volumes from Plankton Counts in Otay Reservoir

Genus	Assumed Geometry		Volumes $((\mu m)^3\ m\ell^{-1})$				
		Date:	6/5	6/23	7/6	8/26	12/1
Anabena	cylinder, 9 μm dia.		30	480	935	369	0
Oscillatoria	cylinder, 15 μm dia.		94	188	0	94	0
Spirulina	proportional		0	64	87	47	0
Navicula	cylinder, 5 μm dia.		5	21	51	0	0
Synedra	cylinder, 8 μm dia.		390	12	12	278	0
Scenedesmus	cylinder, 5 μm dia.		17	0	7	102	24
Other (Green)	proportional		0	9	0	24	7
Trachelmonas	sphere, 23 μm dia.		65	188	29	0	29
Chlamydomonas	sphere, 20 μm dia.		82	271	0	0	213
Carteria	sphere, 20 μm dia.		427	1068	1550	238	195
Other (Flagellates)	proportional		300	326	484	0	57
Crustacea	cylinder, 50 μm dia.		6006	10219	15431	18074	2754
Amorphous	proportional to total algae		2581	1752	3024	3169	3758

geometry was not in references 3 or 4. If so, the volumes of these species were assumed to be proportional to the other species in the same group (e.g., blue green algae). These plankton volumes in units of $\mu m^3\ ml^{-1}$ are listed in Table 4.3.2.

The plankton volumes were multiplied by a density of 1 g cm^{-3} (11) and by plankton metal contents from Table 3.3.1 to give plankton metal concentrations. The plankton metal concentration (PMC) is the amount of metal in plankton per unit volume of lake water. These PMC's were divided by the appropriate unfiltered water metal concentrations to give the metal in plankton as a fraction of total in lake water. The fraction of metal in algae was calculated similarly, deleting zooplankton and amorphous counts from the plankton counts. The fractions of metals in plankton and algae in Otay Reservoir are listed in Table 4.3.3 along with concentration factors for each metal. If 1% is considered a significant fraction, then Otay plankton Cu, Zn, and Cd did not account for significant fractions of Cu, Zn, and Cd in lake water.

The greatest plankton counts occurred on 6/15/76 and 11/10/76. If the aqueous and plankton metal concentrations on 6/15 and 11/10 are assumed to be the same as on 6/5 and 12/1, respectively, then Cd, Zn, and Cu in plankton still accounted for less than 1% of the total metals in lake water.

4.4 On the Rate of Metal Uptake by Plankton

In this section three simple integrated rate expressions are used to predict metal uptake by plankton over periods of up to 6 days. The three models considered are progressively more conservative with

Table 4.3.2

Metals in Plankton and Algae as Fractions of Total Metals in Lake Water, Concentration Factors

Date	Fraction of Total	Metal		
		Zn	Cd	Cu
6/5	plankton[1]	2.5×10^{-4}	2.8×10^{-4}	1.5×10^{-5}
	algae[2]	3.3×10^{-5}	3.7×10^{-5}	2×10^{-6}
	CF	2.3×10^{4}	2.7×10^{4}	1.4×10^{3}
7/7	plankton	3.5×10^{-3}	3×10^{-4}	2.2×10^{-4}
	algae	4.8×10^{-4}	4.1×10^{-5}	3.0×10^{-5}
	CF	1.5×10^{5}	1.3×10^{4}	9.4×10^{3}
6/23	plankton	1.0×10^{-3}	1.1×10^{-4}	2.4×10^{-4}
	algae	1.7×10^{-3}	1.9×10^{-5}	
	CF	6.6×10^{4}	7.3×10^{3}	1.6×10^{4}
8/25	plankton	3.7×10^{-4}	7.5×10^{-4}	1.5×10^{-4}
	algae	1.8×10^{-5}	3.7×10^{-5}	7×10^{-6}
	CF	1.5×10^{4}	3.1×10^{4}	6.1×10^{3}
12/1	plankton	3.2×10^{-4}	9.4×10^{-5}	1.4×10^{-5}
	CF	4.4×10^{4}	1.3×10^{5}	2.6×10^{4}
	8µ[4]	1.8×10^{-3}	---[5]	1.7×10^{-3}

Notes:
1. Mass of plankton estimated from plankton counts.
2. Mass of algae estimated from plankton counts.
3. Concentration factor (dimensionless)

$$CF = \frac{\text{concentration of metal in plankton}}{\text{concentration of metal in water}}$$

4. Fraction of metal retained by 8µ filter in plankton.
5. Unacceptable data.

respect to the rate of metal uptake by plankton. The intention is not to imply that actual uptake is described by any of the models, but rather, that it may fall in the range of uptake predictions. Gross primary productivity was estimated as described in Section 2.3.3 and the results for Otay, Morris, and San Vicente Reservoirs are listed in the Appendix. For these calculations it was assumed that all primary production resulted in carbohydrate synthesis according to the equation $nCO_2 + nH_2O = (CH_2O)_n + nO_2$ and that the production rates remained constant. Plankton metal contents from section 3.3 were used in the calculations. Six days was chosen as typical of the log phase of a plankton bloom.

Three simple models for the distribution of metals between algae and solution were considered. The total amount of metal, metal in plankton plus dissolved metal, was assumed constant. It was assumed that metals were either dissolved or taken up by plankton. That is, the only particulate metal was that which was taken up by plankton. In each case it was assumed that metals taken up were not released. The simplest model was that total algal metal content was constant and independent of aqueous metal concentration. Next, total plankton metal content was assumed to be proportional to aqueous metal concentration. In the third case considered, the plankton metal was partioned between adsorbed and organic forms as defined in section 2.4.2. The organic metal was assumed to be proportional to adsorbed metal at the time of formation of the organic matter and constant thereafter while the adsorbed metal was assumed to be in continuous equilibrium with dissolved metal.

Each case is discussed in more detail below.

4.4.1 Plankton Metal Content Constant

There are at least two possible reasons for plankton metal content to be constant with time and independent of aqueous metal concentration. The metal may be essential for growth such that algae must contain X ppm or they will not grow, or will not grow at an optimal rate. Gerloff and Fishbeck (6) found "critical concentrations" of K, Mg, and Ca in several species of green and blue green algae. The algae did not grow at optimal rates if the algal metal concentrations, in $\mu g\ g^{-1}$, were below the critical concentrations. If the algae grow at their optimal rate of growth during the period considered for these calculations the essential metals should be taken up at constant rates. Another possible explanation is that the algae may be saturated with the metal of interest, even at low ambient concentrations.

The rate of decrease in aqueous concentration of metal M caused by algal uptake is

$$-\frac{d[M]}{dt} = RC \qquad (4.4.1.1)$$

where [M] is the aqueous concentration of M in $\mu g\ l^{-1}$, R is production in $g\ l^{-1}\ day^{-1}$, and C is the total plankton metal content in $\mu g\ g^{-1}$. C is the total of adsorbed, organic, and silica metals from Table 2.3.2. If we let $[M]_o$ stand for metal concentration at time zero and t stand for time in days, then

$$[M] = [M]_o - RCt \qquad (4.4.1.2)$$

Sample calculations of equation 4.4.1.2 and all of the other models considered are listed in Table 4.4.1. Figure 4.4.1 shows the concentration-time behavior predicted by each model. The calculations are listed in the appendix.

4.4.2 Total Plankton Metal Content Proportional to Aqueous Concentration

If metal uptake depends on adsorption then the amount of metal taken up will be proportional to the aqueous metal concentration. For example, Riley and Roth (7) found that the metal contents of marine phytoplankton increased with increasing metal concentrations in culture media. If a Langmuir isotherm describes metal ion adsorption on algal surfaces and metal concentrations are low, then the steep quasi-linear part of the isotherm will be relevant and adsorption will be roughly proportional to solution concentration. Ion exchange equilibria may govern uptake of metal M when $[M] << [Ca]$, $[Mg]$, $[Na]$, $[K]$ and pH is constant. Uptake would then be proportional to $[M]$ (8).

Using the same notation as the previous section we have

$$C = k[M] \tag{4.4.2.1}$$

where

$$k = C/[M]_o \tag{4.4.2.2}$$

Then

$$-\frac{d[M]}{dt} = Rk[M]. \tag{4.4.2.3}$$

Thus,

$$[M] = [M]_o \exp(-RCt/[M]_o) \tag{4.4.2.4}$$

4.4.3 Plankton Metal Content Divided Between Adsorbed and Organic Fractions, Uptake Rate Proportional to Aqueous Metal Concentration.

If organic metal is proportional to adsorbed metal when the organic matter is formed but stays constant afterward, and if adsorbed metal is continuously in equilibrium with aqueous metal, then

$$C_{org} = k_1[M] \text{ at time of formation} \quad \text{where } k_1 = C_{org}/[M]_o \qquad (4.4.3.1)$$

$$C_{ads} = k_2[M] \text{ always} \quad \text{where } k_2 = C_{ads}/[M]_o \qquad (4.4.3.2)$$

C_{org} and C_{ads} are the organic and adsorbed fractions, respectively, from Table 2.3.2. If we consider only the effects of metal uptake into the cell interior, then

$$-\frac{d[M]}{dt} = Rk_1[M] \qquad (4.4.3.3)$$

and $[M]_{org.\ uptake} = [M]_o \exp(-Rk_1 t)$ (4.4.3.4)

Solving for M we find that

$$[M] = \frac{[M]_o \exp(-Rt\, C_{org}/[M]_o)}{1 + Rt\, C_{ads}/[M]_o} \qquad (4.4.3.5)$$

4.4.4 Discussion of Calculations

Figure 4.4.1 shows that in some cases even the most conservative uptake model, equation 4.4.3.5, predicted that metal uptake by plankton can reduce metal concentrations by more than 20% in four days. The concentration factor, also shown in Figure 4.4.1, had to be above about 10^5 to predict noticable reductions in aqueous concentrations. A 20% reduction in aqueous concentration would be easily detected by AAS if the concentrations were sufficiently higher than the detection limit. Thus the predicted reductions in Zn, Mn, and Fe concentrations in Morris and San Vicente Reservoirs would have been detectable. Only the San Vicente Cd reduction would have been unambiguously detectable. Even if a predicted reduction were 1%, that would mean that the fraction of total metal in lake water associated with plankton would be more than ten times greater than

Table 4.4.1

Sample Calculations of Cd Uptake in San Vicente Reservoir 1/19/77

$[Cd] = .001\ \mu g\ \ell^{-1}$	initial aqueous concentration
$R = 3.7 \times 10^{-4} g\ \ell^{-1}\ day^{-1}$	primary production
$C_{tot} = 1.03\ \mu g\ \ g^{-1}$	total Cd content of plankton
$C_{ads} = .915\ \mu g\ \ g^{-1}$	adsorbed Cd content of plankton
$C_{org} = .115\ \mu g\ \ g^{-1}$	organic + silica content of plankton

equation #	equation	6 day prediction
4.4.1.2	$[M] = [M]_o - RCt$	$[Cd] = .001 - (3.7x10^{-4})(1.03)(6) = -.0013$ *
4.4.2.4	$[M] = [M]_o \exp\ (-R \frac{C_{tot}}{[M]_o}\ t)$	$[Cd] = .001 \exp \frac{-(3.7x10^{-4})(1.03)(6)}{.001} = .00010$
4.4.3.5	$[M] = \frac{[M]_o\ \exp(-RtC_{org}/[M]_o)}{1 + RtC_{ads}/[M]_o}$	$= \frac{.001\ \exp(-(3.7x10^{-4})(6)(115)/(.001))}{1 + (3.7x10^{-4})(6)(.915)/(.001)} = .00026$

---

*A negative concentration at time t means that the concentration reached zero before time t. (See Figure 4.4.1).

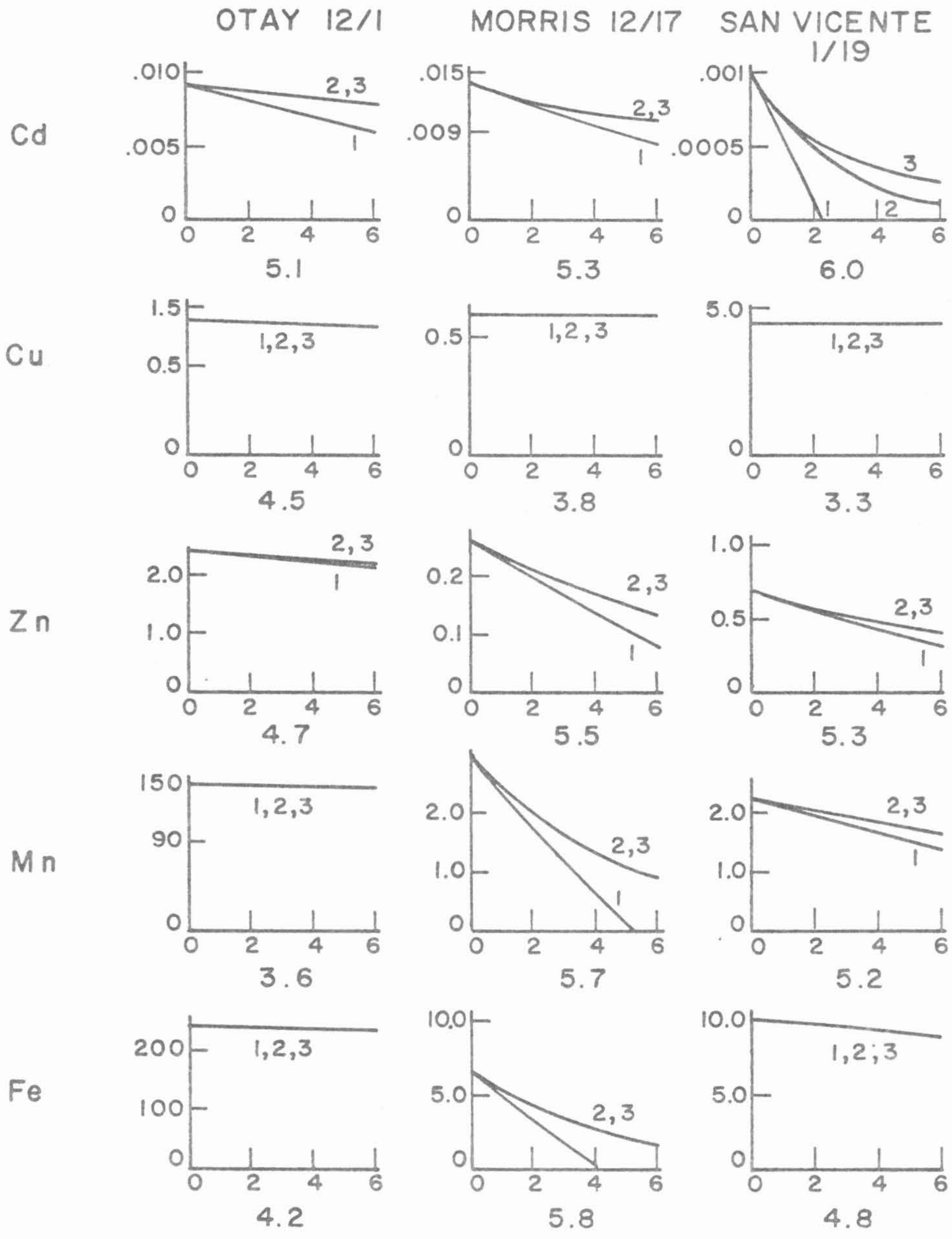
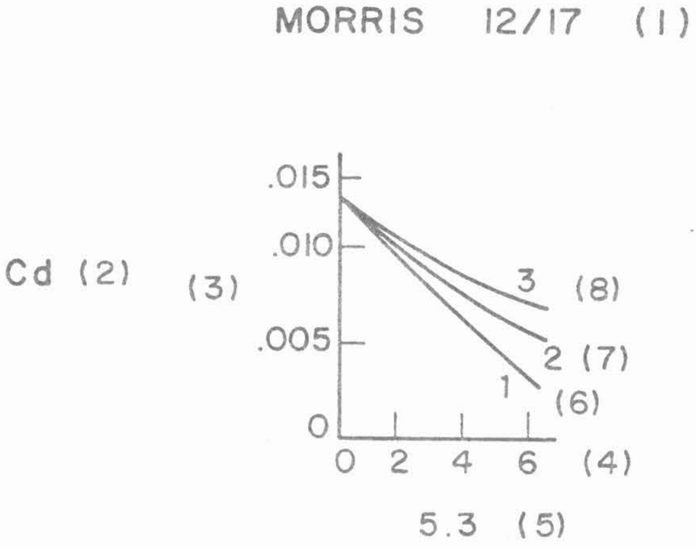


Figure 4.4.1 Predicted Reductions in Metal Concentrations due to Uptake by Plankton. (See Next Page for Notes.)



Notes: (1) Lake from which parameters were obtained (columns)

(2) Metal (rows)

(3) Metal Concentration ($\mu g \ \ell^{-1}$

(4) Time (days)

(5) Log of Concentration Factor

(6) (Number 1) Equation 4.4.1.2

(7) (Number 2) Equation 4.4.2.4

(8) (Number 3) Equation 4.4.3.5

Figure 4.4.1 (Continued) explanations of features of graphs.

that calculated in section 4.3. For example, Figure 4.4.1 shows the Cd concentration being reducted by 30% in one day. This suggests that there was a turnover of Cd in algae and that a significant fraction (i.e. 30%) of the Cd in the lake water was associated with algae some time during that day. Otay plankton did not concentrate Cu, Zn, Mn, or Fe enough to predict observable reductions in concentration of any of these metals.

If Morris and San Vicente plankton contained similarly small fractions of total Cd, Cu, Zn, Mn, and Fe in lake water, then there may have been large turnovers in plankton Cd, Zn, and Mn in both lakes. Fe turnover may have been large in Morris Reservoir but moderate in San Vicente. Cu was not predicted to turn over in any of the lakes because plankton did not concentrate Cu as much as the other metals.

The rate of decrease in concentration correlated with the concentration factor. Manganese is a case in point. Otay plankton, for which the Mn concentration factor (CF) was 4000, reduced the Mn concentration by less than 2% after six days. San Vicente plankton, with a Mn CF of 160,000 reduced the Mn concentration by 31% in six days. Morris plankton, with a Mn CF of 500,000, reduced dissolved Mn by 66% in six days. This is to be expected, of course, since sorption by algae was by definition the only sink for dissolved metals.

Equation 4.4.3.5 predicted lower concentration reductions than equation 4.4.2.4 in only one case, Cd in San Vicente. This was the only case for which the concentration factor and the ratio C_{ads}/C_{org} were high enough for this to happen.

4.5 A Model of Trace Metal Chemistry in Lakes: Comparing Predictions with Observations.

Schindler (11) has proposed a model of regulation of trace metal concentrations in lakes and in the ocean. His model assumes that all particles can be treated as a single solid phase and that the distribution of metal ions between solid and solution phases can be described by a distribution coefficient

$$D = \frac{[M]_p}{[M]A} \qquad (4.5.1)$$

where $[M]_p$ is the amount of metal M associated with particles per liter, $[M]$ is the concentration of dissolved M, and A is the amount of particulate matter per liter. In this work A was taken to be the mass of material retained by a 0.4 µm Nuclepore filter when one liter of sample was filtered.

Schindler derived his model for perfectly mixed lakes at steady state with respect to the flux of water. In the opinion of the author, very few large lakes, like San Vicente Reservoir, which is the test case in this work, are well mixed. Also, San Vicente is a water supply reservoir whose storage is constantly changing, so it is not at steady state with respect to the flux of water. The equations can easily be modified to cover the non-steady state case, though. The non-well-mixed condition will be ignored.

In the following discussion parameters describing the lake's influent will have i subscripts. Effluent flux will have an e subscript. Lake parameters will not have subscripts.

The sedimentation rate of particles, S, is given by

$$S = \phi_i A_i - \phi_e A + B \qquad (4.5.2)$$

where ϕ is the flux of water and B is the rate of in situ production of particulate matter. In this work the primary production measurement was used for B. Equation 4.5.1 says that the difference between the rate of introduction of particulate matter into the lake, $\phi_i A_i + B$, and the rate of particulate matter flowing out of the lake, $\phi_e A$, is due to sedimentation. Thus, since the distribution coefficient describes the distribution of metal ions between solid and solution phases, the rate of metal M sedimenting with the particulate matter is

$$S_M = (\phi_i A_i - \phi_e A + B)\, D\, [M] \qquad (4.5.3)$$

S_M can also be calculated from the mass balance on M if we first note that

$$[M]_t = [M] + [M]_p \qquad (4.5.4)$$

and that, from equation 4.4.1

$$[M]_{tot} = [M]\,(1 + AD). \qquad (4.5.5)$$

Thus,

$$S_M = [M]_i \phi_i\,(1 + A_i D_i) - [M]\phi\,(1 + AD) \qquad (4.5.6)$$

In other words, the metal carried in by the influent stream is either removed by sedimentation or is carried out by the effluent stream.

Equating the expressions for S_M in equations 4.5.3 and 4.5.6 and solving for [M] we obtain a formula for the concentration of dissolved metal.

$$[M] = [M]_i \; \frac{\phi_i\,(1 + A_i D_i)}{(\phi_i A_i + B)\, D + \phi_e} \qquad (4.5.7)$$

By combining equations 4.5.5 and 4.5.7 we obtain a formula for total metal concentration.

$$[M]_t = [M]_{i,t} \frac{\phi_i (1 + AD)}{(\phi_i A_i + B) D + \phi_e} \qquad (4.5.8)$$

The parameters used in the calculations described in the following sections can be found in the appendix.

4.5.1 Sedimentation Rates of Metals

Table 4.5.1 lists sedimentation rates of metals in San Vicente Reservoir calculated from the observed flux of particles, metal content of the particles, and the surface area of the lake, assuming that sedimentation flux was uniform over the entire lake. Sedimentation rates were also calculated from equations 4.5.1 and 4.5.2 and are also listed in table 4.5.1.

There was agreement within a factor of two between observed and predicted Cd sedimentation rates in three cases. Two of the Cu and two of the Zn predictions were close to the observed values, while none of the Mn predictions were within a factor of two of the observed values. Section 4.5.4 shows why agreement within a factor of two can be considered good agreement.

4.5.2 Dissolved Metals

Predicted and observed dissolved metal concentrations are listed in Table 4.5.2. The Cu predictions for both sampling dates were within a factor of two of observed filtered Cu concentrations. For Cd, Zn, and Mn one prediction was close and the other was low by an order of magnitude.

Table 4.5.1

Calculated and Observed Sedimentation Rates of Metals in San Vicente Reservoir (μg day^{-1})

	Observed	Calc. from Part. Mass Bal.[1]		Calc. from Met. Mass Bal.[2]	
		1/19	1/26	1/19	1/26
Cd	1.61	<2.73	3.04	1.93	-.55
Cu	112.	164.	8.6	702.	115.
Zn	211.	3040.	272.	-13.7	126.
Mn	22800.	4040.	2830.	5390.	-560.

Notes: 1. $S_{M,P} = (\phi_i A_i - \phi_e A + B) D [M]$

2. $S_{M,M} = [M]_i \phi_i (1 + A_i D_i) - [M]\phi(1 + AD)$

Table 4.5.2

Calculated[1] and Observed Dissolved Metal Concentrations

($\mu g\ \ell^{-1}$)

	Observed		Calculated	
	1/19	1/26	1/19	1/26
Cd	<.0002	.0021	.00015	<.00015
Cu	4.51	.49	6.23	.90
Zn	.69	1.04	.068	.94
Mn	2.24	3.35	1.23	.57

Notes: 1. $[M] = [M]_i \dfrac{\phi_i\ (1 + A_i D_i)}{(\phi_i\ A + B)D + \phi_e}$

4.5.3 Total Metals

Schindler's ultimate prediction in his lake model is the relative residence time of metals. Since this was not directly measurable, equation 4.5.7 for total metal concentration was compared with observed unfiltered water metal concentrations. The results are shown in Table 4.5.3. The 1/19 Cd prediction was high by an order of magnitude while the 1/26 prediction was within a factor of 2.5 of the observed value. Both Cu predictions were close to observed total Cu concentrations. Both Mn predictions and the single Zn prediction were very close to measured total concentrations. Overall, 60% of the model's predictions agreed with observations of Cu, Zn, Cd, and Mn concentrations and sedimentation rates. Manganese chemistry is probably controlled by redox processes as well as adsorption, so Schindler's model is not expected to predict Mn behavior adequately. If only Cu, Zn, and Cd are considered, then 70% of the model's predictions agree with observations.

4.5.4 Errors in Predictions

For a function $\mu = \mu(z,y,z,\ldots)$

$$d\mu = \frac{\partial \mu}{\partial x}\,dx + \frac{\partial \mu}{\partial y}\,dy + \frac{\partial \mu}{\partial z}\,dz + \ldots \qquad (4.5.4.1)$$

If the errors in x,y,z,... are small enough, i.e. a "few percent" (12), the error in μ, $\Delta\mu$, is

$$\Delta\mu = \frac{\partial \mu}{\partial x}\,\Delta x + \frac{\partial \mu}{\partial y}\,\Delta y + \frac{\partial \mu}{\partial z}\,\Delta z + \ldots \qquad (4.5.4.2)$$

The errors in the parameters measured for Schindler's model, particularly B and (Cd), are probably greater than a few percent, but the error bounds may be useful in distinguishing "good" predictions

Table 4.5.3
Calculated[1] and Observed Total Metal Concentrations[2]

	Observed		Calculated	
	1/19	1/26	1/19	1/26
Cd	<.0002	.003	.002	.0068
Cu	4.54	.49	7.0	1.1
Zn	--	1.11	--	1.1
Mn	13.8	6.26	12.0	8.9

Notes: 1. $$[M]_t = [M]_{i,t} \frac{\phi_i \ (1 + AD)}{(\phi_i \ A_i + B) \ D + \phi_e}$$

2. $\mu g \ \ell^{-1}$

from "bad" ones. Listed below are the predictive equations from sections 4.5.1 through 4.5.3 and the predicted errors obtained by applying equation 4.5.4.2 to them.

$$S_M = (\phi_i A_i - \phi_e A + B) D [M] \qquad (4.5.2)$$

$$\Delta S_M = [M]_i \phi_i A_i \Delta D_i + \phi_i (1 + A_i D_i) \Delta [M]_i + [M] \phi_e \Delta D + \phi_e (i + AD) \Delta [M] \qquad (4.5.4.3)$$

$$SM = [M]_i \phi_i (1 + A_i D_i) - [M] \phi_e (1 + AD) \qquad (4.5.3)$$

$$\Delta S_M = [M]_i \phi_i A_i \Delta D_i + \phi_i (1 + A_i D_i) \Delta [M]_i + [M] \phi_e \Delta D + \phi_e (1 + AD) \Delta [M] \qquad (4.5.4.4)$$

$$[M] = [M]_i \frac{\phi_i (1 + A_i D_i)}{(\phi_i A_i + B) D + \phi_e} \qquad (4.5.4)$$

$$\Delta [M] = [M]_{calc} \left(\frac{\Delta [M]_i}{[M]_i} + \frac{A_i \Delta D_i}{1 + A_i D_i} + \frac{D \Delta B + (\phi_i A_i + B) \Delta D}{(\phi_i A_i + B) D + \phi_e} \right) \qquad (4.5.4.5)$$

where $[M]_{calc}$ is obtained from equation 4.5.4.

$$[M]_t = [M]_{i,t} \frac{\phi_i (1 + AD)}{(\phi_i A_i + B) D + \phi_e} \qquad (4.5.7)$$

$$\Delta[M]_t = [M]_{t,\ \mathrm{calc}} \left(\frac{\Delta\ [M]_{i,t}}{[M]_{i,t}} + \frac{D\Delta B}{(\phi_i A_i + B)\ D + \phi_e} + \frac{\Delta D}{1 + AD} \quad \frac{\phi_e\ A - \phi_i\ A_i\ -\ B}{(\phi_i\ A_i\ +\ B)\ D + \phi_e} \right) \qquad (4.5.4.6)$$

Relative errors in ϕ, ϕ_i, A, and A_i were assumed to be much smaller than the relative errors in $[M]_i$, D, D_i, and B. The error expressions can be simplified by noting that with a consistent set of units the orders of magnitude of the various parameters are

$A = 10^{-3}$ to 10^{-2} g ℓ^{-1} $\qquad$ $D = 10^1$ to 10^3 ℓ g^{-1}

$B = 10^6$ g day^{-1} $\qquad$ $\phi = 10^8$ ℓ day^{-1}

The expressions for relative error become

$$\frac{\Delta S_M}{S_M} \cong \frac{\Delta B}{B} + \frac{\Delta D}{D} + \frac{\Delta[M]}{[M]} \qquad (4.5.4.7)$$

$$\frac{\Delta[M]}{[M]} \cong \frac{\Delta[M]_i}{[M]_i} + A_i \quad D_i + \frac{\Delta B}{B} + \frac{\Delta D}{D} \qquad (4.5.4.8)$$

$$\frac{\Delta[M]_t}{[M]_t} \cong \frac{\Delta[M]_{i,t}}{[M]_{i,t}} + \frac{\Delta B}{B} + \frac{\Delta D}{D} \qquad (4.5.4.9)$$

The quantity with the greatest uncertainty is B for which the relative error may approach 1. This is why agreement within a factor of two was considered good in comparing theory with observation.

4.6 Summary

This thesis has discussed the influence of aqueous metal concentrations on plankton metal contents and how metal uptake by plankton may influence the concentrations and speciation of metals in lakes.

The relation of aqueous metal concentrations to plankton metal contents was studied by comparing plots of plankton metal contents _vs_ time with plots of aqueous metal concentrations _vs_ time. Alhtough none of the plankton plots were identical to their corresponding aqueous plots with respect to changes in metal concentrations, plankton and aqueous metal concentrations showed overall increases from June to December. The overall increases in plankton metal concentrations, however, were greater than the increases in aqueous metal concentrations. Thus, while passive sorption may be partly responsible for metal uptake by plankton, other mechanisms, such as active uptake, are probably also important. The surface properties of plankton may change with time as the species composition changes and this may also influence metal uptake. The fact that no plankton pattern was identical to its corresponding aqueous pattern with respect to short term changes in metal concentration indicates that the ability of plankton in a given lake to concentrate metals was not constant over periods as short as two weeks.

There was similarity between plankton metal patterns. In Morris Reservoir three groups of metals containing four, three, and two metals, respectively, followed identical patterns of changes in plankton metal contents. In Otay Reservoir groups of four, two, and two metals followed identical patterns of changes in plankton metal content. Random fluctuations did not explain the variations in plankton metal concentrations because there would have been less grouping of patterns. The groupings cannot be explained by similarities in aqueous chemistry of the metals, either. For example, one group of metals in Morris plankton consisted of Cd, Co, Al, and Na. In this group ionic charges range from +1 to +3. Cd and Co are strong adsorbers while Na is not. Cd, Co, and Al hydrolize while Na does not. There may be physiological reasons for the groupings of metals.

The amounts of Cu, Zn, and Cd associated with plankton per liter of water, $[M]_{pl}$, were calculated for each Otay sample. It was found that $[M]_{pl}$ was less than 1% of $[M]_{tot}$, the total metal concentration, for all three metals in all samples. Thus, plankton metals should make up only a small fraction of metals found in solid phases. In fact, Table 4.3.2 shows that plankton Zn and Cu comprised less than 0.2% of the Zn and Cu in particles caught by an 8 μm filter.

The rates of depletion of aqueous metal concentrations by plankton metal uptake were calculated using three integrated rate equations as models of plankton metal uptake. The object of the calculations was to see whether metal uptake by plankton could cause measurable reductions in aqueous metal concentrations. The parameters used in the model equations were obtained from analyses of field samples. It was found that when the concentration factor was greater than 10^5, plankton metal uptake was predicted by equation 4.4.3.5, the equation which is the most conservative with respect to the amount of metal sorbed, to reduce aqueous concentrations by more than 20%, a measurable amount, within four days. This would mean that at the end of four days at least 20% of the total metal would be associated with plankton. However, the fraction of total metal in plankton was found to be less than 1% of $[M]_{tot}$ in all cases, so the rates of release of metals from plankton were roughly equal to the rates of uptake.

The importance of plankton in trace metal chemistry in lakes was illustrated by a model proposed by Schindler. The model considers all solids to be a single phase and assumes that metal ions are distributed between solution and solid phases according to a distribution coefficient which is constant at a given solution composition including pH, concentrations of major cations, and concentrations of ligands. A term for the rate of *in situ* production of particulate matter is included and primary production was used for this parameter. In San Vicente Reservoir, the test case considered in this thesis, the *in situ* rate of production of particulate matter was of the same order of magnitude as the rate of introduction of particulate matter by the influent stream. Thus, since solids control aqueous metal concentrations and since the biota produce solids at a rate comparable to the rate of introduction of influent solids, the biota play a significant role in trace metal chemistry. The model's predictions agreed with observations within error bounds based on measurement errors in about two thirds of the cases considered.

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APPENDICES

Appendix A

Otay Reservoir Plankton Counts[1,2]

Date:	5/18	5/25	6/2	6/8	6/15	6/22	6/29	7/7	7/14
Blue Green Algae									
Anabena	77	9	9	51	119	144	289	281	21
Oscillatoria	9	0	17	0	60	34	0	0	17
Spirulina	0	0	0	0	0	17	0	26	38
Diatoms									
Navicula	0	0	4	0	0	17	0	43	0
Synedra	4	0	132	68	94	4	4	4	68
Other[3]	0	0	0	0	0	0	0	21	0
Dinoflagellates									
Peridinium	0	0	17	13	0	47	21	0	9
Other[3]	0	0	0	13	0	0	0	4	0
Green Algae									
Scenedesmus	0	0	9	0	4	0	0	4	9
Other[3]	0	4	0	4	0	4	0	0	0
Pigmented Flagellates[4]									
Trachelmonas	13	0	9	0	4	26	9	4	0
Chlamydomonas	0	0	13	0	4	43	0	0	0
Carteria	535	136	68	21	542	170	153	247	30
Other[3]	17	17	47	38	77	47	220	77	77
Crustacea	655	183	325	208	900	553	749	835	290
Amorphous	361	510	595	574	563	404	446	680	574

Appendix A (Continued)

Otay Reservoir Plankton Counts[1,2]

Date:	7/20	7/27	8/3	8/11	8/17	8/25	9/1	9/15	9/22
Blue Green Algae									
Anabena	17	9	43	102	68	111	162	9	17
Oscillatoria	26	0	26	0	9	17	55	4	9
Spirulina	0	0	34	9	0	13	72	9	4
Diatoms									
Navicula	0	9	9	17	9	0	9	0	4
Synedra	127	13	0	0	4	94	21	38	0
Other[3]	0	0	4	0	0	0	4	0	0
Dinoflagellates									
Peridinium	0	0	0	4	0	0	9	0	0
Other[3]	0	0	0	0	0	0	0	0	0
Green Algae									
Scenedesmus	4	0	0	9	13	55	13	9	9
Other[3]	0	0	9	0	4	13	9	4	0
Pigmented Flagellates[4]									
Trachelmonas	0	0	0	0	0	0	0	0	0
Chlamydomonas	47	4	17	9	9	0	4	38	9
Carteria	0	13	4	26	0	38	0	0	9
Other[3]	13	0	0	39	0	0	0	0	8
Crustacea	234	48	193	215	120	341	349	128	73
Amorphous	893	850	978	563	1148	978	765	925	701

Appendix A (Continued)

Otay Reservoir Plankton Counts[1,2]

Date:	9/29	10/5	10/20	11/10	11/17	12/1
Blue Green Algae						
Anabena	0	0	9	0	0	0
Oscillatoria	0	60	9	0	0	0
Spirulina	0	21	0	0	0	0
Diatoms						
Navicula	0	0	0	0	0	0
Synedra	13	170	9	0	0	0
Other[3]	0	21	0	0	0	0
Dinoflagellates						
Peridinium	0	0	0	0	0	0
Other[3]	0	9	0	0	0	0
Green Algae						
Scenedesmus	17	4	9	13	4	13
Other[3]	61	0	9	30	0	4
Pigmented Flagellates[4]						
Trachelmonas	0	0	0	0	0	4
Chlamydomonas	9	17	30	0	0	34
Carteria	9	89	144	680	9	31
Other[3]	4	64	17	30	123	9
Crustacea	113	540	236	753	136	149
Amorphous	893	893	1233	1105	723	680

Appendix A (Continued)

Notes

1. Counts taken by San Diego, California. Water Utilities Department.

2. Units are Standard Units per Milliliter (S)

$$S \div 4.25 = \mu m^2\ ml^{-1}$$

3. A genus was lumped with "other" if it occurred infrequently in the plankton counts. Included under this heading were:
   Diatoms - _Stephanodiscus_, _Fragilaria_
   Green Algae - _Pediastrum_, _Staurastrum_, _Closterium_
   Pigmented Flagellates - _Halderia_

4. This category was called "protozoa" on the plankton count forms.

Appendix B

Hydrologic Data for San Vicente Reservoir[1]

January, 1977

Flow In: 3052.0 x 10^6 gallons

Flow Out: 2072.0 x 10^6 gallons

Capacity: 29401.7 x 10^6 gallons

Area: 1069 acres

Note: Data furnished by San Diego, California Water Utilities Department.

Appendix C

Raw Data From Solids Analyses

Table C-1. Weight of Samples[1]

Otay Reservoir Date:	6/5	6/23	7/6	8/26	12/1
Sample					
Plankton Fresh[2]	4.1	8.69	2.2	2.6	1.06
Plankton Dry[2]	--[3]	0.56	0.2	--	0.10
Digested Plankton[7]	1.06	0.28	0.17	0.33	0.17
Plankton SiO_2[4] (d)[5]	0.0228	--	0.0028	0.0116	0.0231

Morris Reservoir Date:	6/28	8/20	11/17	12/17
Sample				
Plankton Fresh	22.9	2.6	1.64	1.44
Plankton Dry	--	0.3	0.11	0.12
Digested Plankton (d)	1.12	0.19	0.18	3.28 (f)[5]
Plankton Adsorbed[8] (f)	--	--	--	1.80
Sedimenting Particles[6] (f)	10/7 - 11/17 total 33.5			
Sedimenting Particles[6] (f)	7/20 - 8/20 total 2.35			
Sedimenting Particles[6] (f) Digest[7]		10/7-11/17 1.45 (f)		
Sedimenting Particles[6] (f) Digest[7]		7/20 - 8/20 .07 (d)		
Plankton SiO_2 (d)	0.42	0.0068	0.0367	0.0193

Hodges Reservoir Date:	7/7	8/25
Sample		
Plankton Fresh	7.5	3.3
Plankton Dry	1.0	0.5
Digested Plankton (d)	0.69	0.36
Plankton SiO_2 (d)	0.0062	0.0062

Castaic Reservoir Date: 1/10

Sample		
Suspended Solids (mg ℓ^{-1})[9] (d)	0.4 µm	8.0 µm
S1	2.44	7.40
S2	1.89	6.73

Appendix C (Continued)

Raw Data From Solids Analyses

Table C-1. Weight of Samples[1] (Continued)

San Vicente Reservoir	Date:	1/19	1/26
Sample			
Plankton Fresh		0.56	--
Plankton Dry		0.06	--
Digested Plankton (d)		0.43	--
Plankton Adsorbed (f)		0.60	--
Sedimenting Particles (f)		--	1.04
Suspended Solids (mg ℓ^{-1}) (d)			
0.4 μm influent		0.36	1.80
8.0 μm influent		1.20	6.30
0.4 μm lake		0.34	0.73
8.0 μm lake		0.43	0.88

San Dieguito Reservoir	Date:	6/23
Sample		
Total Plankton Sample (f)		17.9
Digested Plankton Sample (f)		1.4
Plankton SiO_2		0.0095

Appendix C

Raw Data From Solids Analyses

Table C-2. Volumes of Digests[10]

Otay Reservoir	Date: 6/5	6/23	7/6	8/26	12/1
Sample					
Plankton Organic Fraction	9.8	21.9	14.2	9.7	13.1
Plankton SiO_2 Fraction	5.0	--	5.0	5.0	2.0
Plankton 1st Adsorbed Fraction	--	--	--	--	28.7
Plankton 2nd Adsorbed Fraction	--	--	--	--	28.5
Suspended Solids 0.4 µm ads[16]	--	--	--	--	29.0
Suspended Solids 8.0 µm ads	--	--	--	--	29.1
Suspended Solids 0.4 µm org[17]	--	--	--	--	8.5
Suspended Solids 8.0 µm org	--	--	--	--	16.6

Morris Reservoir	Date: 6/28	8/20	11/17	12/17
Sample				
Plankton 1st Adsorbed Fraction	--	--	21.1	25.3
Plankton 2nd Adsorbed Fraction	--	--	25.3	25.6
Plankton Organic Fraction	12.7	12.6	9.7	9.89
Plankton SiO_2 Fraction	5.0	5.0	4.0	5.0
Suspended Solids 0.4 µm ads	--	--	27.6	15.0
Suspended Solids 8.0 µm ads	--	--	25.6	15.2
Suspended Solids 0.4 µm org	--	--	7.4	6.7
Suspended Solids 8.0 µm org	--	--	7.3	8.1
Sediment Organic Fraction	8/20	11.0		
Sediment Organic Franction	11/17	12.8		

Hodges Reservoir	Date: 7/7	8/25
Sample		
Plankton Organic Fraction	12.5	12.7
Plankton SiO_2 Fraction	5.0	5.0

Castaic Reservoir	Date: 1/10	1/24	1/24
Sample	Station: S1	S1	S2
Suspended Solids 0.4 µm ads	9.5	13.9	15.3
Suspended Solids 8.0 µm ads	10.6	11.1	14.8

Appendix C

Raw Data From Solids Analyses

Table C-2. Volumes of Digests[10] (Continued)

Castaic Reservoir	Date:	1/10	1/24	1/24
Sample	Station:	S1	S1	S2
Suspended Solids 0.4 μm org		5.2	5.6	6.6
Suspended Solids 8.0 μm org		5.7	5.1	5.3

San Vicente Reservoir	Date:	1/19	1/26		
Sample					
Plankton Adsorbed Fraction		15.0	--		
Plankton Organic Fraction		6.0	--		
Plankton SiO_2 Fraction		4.0	--		
Sediment Organic Fraction		--	10.7		
Suspended Solids	Station:	I	L	I	L
0.4 μm ads		17.0	14.0	--	--
8.0 μm ads		12.4	13.8	--	--
0.4 μm org		6.6	4.6	5.5	5.6
8.0 μm org		5.2	5.0	4.7	5.4

Appendix C (Continued)

San Dieguito Reservoir

Sample	Date: 6/23
Plankton Organic Fraction	12.5
Plankton SiO_2 Fraction	5.0

Table C-3. Metal Concentrations in Plankton and Sediment Digests[11]

Sample	Cd	Pb	Co	Cu	Zn	Mn	Fe	Na	K	Mg	Ca	Sr	Ba	Al
0, 6/5, 0	5.4	3.39	22.8	.315	2.29	--	15.4	477	905	289	1520	--	--	8.62
0, 6/5, S	1.88	5.56	ND[13]	.037	.063	.806	3.53	--	--	--	--	--	--	24
0, 6/24, 0	.91	2.5	5.7	.26	.84	8.26	7.13	33.5	123	16.3	153	--	--	--
0, 7/6, 0	.842	12.7	7.55	.254	1.75	9.35	13.8	26.3	109	18.8	204	3.88	5.86	6.0
0, 7/6, S	.198	ND	4.72	.059	ND	5.07	2.36	--	1.30	3.37	13.0	.278	--	12.5
0, 8/26, 0	5.39	ND	19.6	.194	.582	10.1	10.0	153	438	110	371	--	--	1.6
0, 8/26, 0	1.03	ND	ND	.37	.343	3.77	--	--	--	--	--	--	--	22.8
0, 12/1, A1	5.07	36.6	38.8	.043	.63	5.14	.973	9.8	284	41.8	101	13.5	8.35	ND
0, 12/1, A2	.96	8.78	11.3	.036	.068	.46	.351	--	--	--	--	--	--	--
0, 12/1, 0	2.38	62.9	18.6	.396	.218	.607	50	48.5	24.1	60.5	134	2.23	ND	280
0, 12/1, S	.215	14.2	16.0	.026	.025	.287	11.8	--	--	--	--	--	--	107
M, 6/28, 0	ND	ND	ND	ND	.183	15.8	13.0	56.7	100	58	285	--	--	10.5
M, 6/28, S	ND	5.56	ND	.037	.063	5.26	--	--	--	--	--	--	--	37.5
M, 8/20, 0	1.24	29.8	9.43	.70	.96	7.27	37.5	18.5	14.3	20.3	218	4.07	7.55	20
M, 8/20, S	.198	7.32	7.55	.098	.30	5.07	8.47	--	6.85	5.62	8.3	.741	--	42
M, 11/17, A1	36.5	113	72.5	.057	.402	2.93	2.25	29.8	55.5	12.6	19.6	1.34	1.67	1.93
M, 11/17, A2	12.1	29.5	19.2	.029	.060	.30	.891	2.94	7.33	1.52	3.8	ND	ND	ND
M, 11/17, 0	ND	7.36	24.2	.285	.540	1.40	95.0	4.15	27.3	5.30	13.7	.319	ND	104
M, 11/17, S	13.1	27.1	8.33	.014	.026	.247	15.0	--	--	--	--	1.59	2.78	115
M, 12/17, A1	15.1	17.4	44.2	.010	6.72	3.31	2.19	7.35	12.8	3.73	28.0	.26	ND	.77
M, 12/17, A2	--	7.67	--	.009	--	0.38	0.36	1.47	3.53	.82	4.50	ND	ND	.77
M, 12/17, 0	37.5	26.2	32.7	.248	21.9	9.58	92.3	30.0	200	43.4	63.5	.13	11.4	83.9
M, 12/17, S	.8	ND	19.3	.024	1.78	0.78	21.5	62.6	52.3	9.85	27.5	--	8.5	123

Appendix C (Continued)

Sample	Cd	Pb	Co	Cu	Zn	Mn	Fe	Na	K	Mg	Ca	Sr	Ba	Al
H, 7/7, O	7.38	27.8	26.4	.84	1.88	11.3	35.6	243	467	60.7	147	3.50	6.21	31.0
H, 7/7, S	.25	.97	ND	.059	.14	1.13	.69	--	.74	.5	.75	ND	--	3.5
H, 8/25, O	5.83	10.7	15.1	.436	1.06	4.11	40.6	26.3	109	29.4	88.5	2.03	5.52	37.0
H, 8/25, S	ND	ND	5.66	.033	.12	2.82	7.08	--	3.7	2.25	5.53	3.70	--	33.0
D, 6/23, O	2.52	39.5	23.6	2.1	--	5.92	19.1	25.1	93.9	26.5	40.0	3.93	31.7	21.0
D, 6/23, S	ND	7.8	ND	.064	ND	1.13	1.25	--	3.15	1.13	1.28	1.48	--	31.0
S, 1/19, A	5.33	6.71	27.7	.026	.006	.82	.22	5.41	21.7	3.04	7.54	--	--	--
S, 1/19, O	8.25	13.6	19.1	.121	2.04	12.7	5.21	135	342	47.2	76.0	7.9	5.7	40.0
S, 1/19, S	ND	ND	2.8	.005	ND	.19	.94	2.63	2.52	.86	.17	ND	ND	4.6
Sediments														
M, 7/15, O	4.0	49.7	46.2	.19	.44	10.9	170	4.06	41.7	87.0	720	7.63	ND	111
M, 11/17, O	12.2	60.0	94.6	2.41	4.47	105	1940	6.0	576	877	953	19.5	108	331
S, 1/19, O	8.67	22.9	85.4	.60	1.14	123	600	5.59	117	190	169	7.37	25.0	281

Appendix C (Continued)

Table C-4. Metal Concentrations in Filter Digests[14]

Sample	Cd	Pb	Cu	Zn	Fe	Mn	Na	K	Mg	Ca
M, 11/17, 4, A	ND	2.5	ND	ND	22.0	40.0	ND	ND	.03	.29
M, 11/17, 8, A	ND	3.5	11.2	ND	44.0	93.0	ND	ND	.06	.89
M, 11/17, 4, O	.13	8.4	24.6	14.0	1470	146	.17	.25	.38	.10
M, 11/17, 8, O	.17	5.9	71.6	11.0	4230	259	.25	.86	1.48	.44
M, 12/17, 4, A	.054	2.3	2.59	ND	228	167	.09	.04	.11	1.40
M, 12/17, 4, O	.19	13.0	4.30	8.58	1073	101	--	--	--	--
M, 12/17, 8, O	.11	11.3	3.58	19.7	3152	275	--	--	--	--
O, 12/1, 4, O	ND	1.50	ND	ND	ND	--	--	--	--	--
O, 12/1, 8, O	ND	1.10	ND	ND	51.0	ND	--	--	--	--
O, 12/1, 4, A	.38	2.40	.89	10.2	1430	285	--	--	--	--
O, 12/1, 8, A	.27	5.50	5.80	17.5	3900	892	--	--	--	--
SL, 1/19, 4, A	ND	1.80	.42	4.30	13.0	15.0	.12	ND	.10	.17
SL, 1/19, 8, A	ND	.92	.85	3.33	20.3	54.1	.10	ND	.11	.38
SL, 1/19, 4, O	.80	3.20	ND	3.33	941	54.1	.12	.06	.20	ND
SL, 1/19, 8, O	.54	2.30	ND	3.54	941	107	.05	.10	.25	ND
SI, 1/19, 4, A	ND	ND	ND	2.28	ND	10.3	.14	ND	.11	.30
SI, 1/19, 8, A	ND	ND	ND	2.73	9.70	17.9	.16	ND	.13	.34
SI, 1/19, 4, O	.40	4.60	.28	2.17	599	32.6	.10	.10	.19	ND
SI, 1/19, 8, O	ND	2.80	.56	2.27	--	37.1	.20	.06	.20	ND
SI, 1/26, 4, T	.125	3.16	ND	19.5	3060	196	1.24	.81	1.59	1.61
SI, 1/26, 8, T	.333	2.76	ND	1.25	1280	59.0	.62	.38	.87	1.27
SL, 1/26, 4, T	.083	1.78	ND	.88	280	20.0	.97	.05	.43	.51
SL, 1/26. 8, T	ND	2.96	ND	5.0	540	78.0	.64	.17	.72	.42
C1, 1/10, 4, A	ND	1.15	3.40	1.97	81.9	37.0	ND	--	.11	1.12
CI, 1/10, 8, A	ND	1.10	2.38	3.19	123	55.6	.12	--	.28	5.58
CI, 1/10, 4, O	ND	2.71	1.43	10.2	1560	29.6	ND	--	.56	ND
CI, 1/10, 8, O	.054	2.31	1.07	8.0	4220	37.0	ND	--	1.21	ND
CI, 1/24, 4, T	ND	5.13	1.99	18.3	4470	59.0	.29	1.06	1.09	.085
CI, 1/24, 8, T	ND	5.33	2.21	15.4	4540	59.0	.083	.91	1.16	.085
C2, 1/24, 4, A	.333	1.78	.89	9.50	60.0	59.0	.07	ND	ND	.47
C2, 1/24, 8, A	.417	3.16	1.55	8.50	60.0	78.0	.16	ND	ND	.47
C2, 1/24, 4, O	ND	3.55	.89	9.40	2280	59.0	.11	.36	.58	ND
C2, 1/24, 8, O	ND	3.95	.89	14.3	1890	59.0	--	.28	.72	ND
M, 12/17, 8, A	ND	4.2	2.41	ND	228	167	.09	.04	.11	1.40

Appendix C (Continued)

Notes

1. Weights in grams unless otherwise specified.

2. Sub-sample to determine moisture content.

3. -- indicates no data.

4. SiO_2: the solids that survived the $HNO_3 + HClO_4$ digestion.

5. (d): dry weight
   (f): fresh weight

6. Weight of total sediment sample.

7. Weight of sample digested.

8. Weight of sub-sample treated with dilute HNO_3.

9. Suspended solids were determined by filtering a known volume of lake water through tared filters, lyophilizing the filters, and weighing.
   Size fractions are explained in the text.

10. Volumes in ml.

11. Cd, Pb, and Co concentrations are in $\mu g\ \ell^{-1}$. All other concentrations are in $mg\ \ell^{-1}$.

12. The sample codes are in the following format: Lake, Date, Fraction.
    Lake: O Otay, M Morris, H Hodges, S San Vicente, D San Dieguito.
    Date: Month/day (i.e. 11/17 is November 17).
    Fraction: O organic, A1 first adsorbed, A2 second adsorbed, A adsorbed, S silica.

13. ND: Not detected.

14. In Table C-4 Na, K, Mg, and Ca concentrations are in $mg\ \ell^{-1}$. All other concentrations are in $\mu g\ \ell^{-1}$.

15. The sample codes are similar to those in Table C-3. The format is: Lake, Date, Size, Fraction.
    Lake: SL San Vicente "lake", SI San Vicente "influent", C1 Castaic Station 1, C2 Castaic Station 2.
    Size: 4 0.4 - 8.0 µm.
    8 larger than 8.0 µm.
    Fraction: T total, or A+O.

Appendix C (Continued)

Notes

16. ads stands for adsorbed fraction.

17. org stands for organic fraction.

Appendix D

Metal Concentrations[1] in Water Not Reported in Chapter 3

				Mn	Fe	Na	K	Mg	Ca
Hodges		8/25	T[2]	--	--	--	--	--	52.6
			F[2]	--	--	--	--	--	54.3
Otay		8/26	T	--	--	--	--	--	42.8
			F	--	--	--	--	--	44.2
Otay		12/1	T	.24	.14	126.	43.2	37.2	66.2
			F	.24	.15	--	--	--	--
Morris		11/17	T	.12	.021	14.3	26.5	83.6	53.3
			F	.02	.002	--	--	--	--
Morris		12/17	T	.140	.036	15.8	7.1	72.6	18.6
			F	.007	.003	--	--	--	--
Castaic	S1	1/10	T	.024	.24	52.9	4.8	48.1	18.9
	S1		F	.019	--	--	--	--	--
	S2		T	.014	.16	47.5	4.4	53.7	17.2
	S1	1/24	T	.018	.094	40.4	2.5	90.5	19.0
	S1		F	.011	.018	37.7	2.3	87.5	17.8
	S2	1/24	T	.008	.042	37.7	2.4	90.0	19.0
	S2		F	.007	.009	--	--	--	--
San Vicente	Influent	1/19	T	.012	.021	99.6	5.8	29.4	32.3
			F	.004	.005	102.	5.7	29.0	32.3
	Lake	1/19	T	.014	.002	105.	5.8	29.6	32.3
			F	.012	.021	99.6	5.6	29.0	32.3
San Vicente	Influent	1/26	T	.013	.11	96.9	5.33	28.0	33.5
			F	.001	.009	96.9	5.21	27.6	33.5
	Lake	1/26	T	.006	.076	105.	5.6	29.3	32.3
			F	.003	.008	99.6	5.7	28.7	31.2

Appendix D (Continued)

Notes

1. All concentrrations are in mg ℓ^{-1}.

2. T total, unfiltered water
   F filtered water

Appendix E

Primary Production Measurements

Since some of the precautions listed by Vollenweider (Ref. 10, Chapter 2) for accurate productivity measurements were not feasible (i.e. incubating duplicate bottles, suspending bottles in a horizontal position, ...) the data are somewhat scattered. They, do however, resemble normal productivity profiles. Rather than integrating the raw data numerically a function of the form

$a + a \cos \frac{(Z-1)\,\pi}{Z_{max}-1}$, where a = 1/2 of maximum productivity in

mg O_2 $m^{-3} day^{-1}$, Z = depth in meters, and Z_{max} is the extrapolated depth of the compensation point, was fitted to the data and integrated analytically. The relevant parameters and calculated areal productivity rates are listed in this appendix. It was assumed that all primary production resulted in carbohydrate synthesis according to the equation $6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$.

Appendix E (Continued)

Table E1

Productivity Measurements

Lake	Date	A^1	Z_{max}(m)	R^2
Otay	12/1/76	370	7	1120
Morris	12/17/76	450	8	1530
San Vicente	1/19/77	350	10	1460

Notes: 1. Units of A are mg O_2 m^{-3} $(1/2\ day)^{-1}$.

2. Estimatd gross primary productivity mg C $m^{-2}day^{-1}$.

APPENDIX F

Equilibrium Speciation of Cu, Zn, and Cd in Lake Water

		Ligand:	CO_3	CL	SO_4	F	NH_3	PO_4	SAL	GLY	PATH	OH
	Total	→	2.90	3.50	3.90	5.50	5.50	5.00	5.00	7.00	6.00	--
Metal	↓	Free → ↓	5.02	3.49	4.01	5.53	6.54	12.12	10.86	8.89	6.10	6.00
Zn	7.30	7.32	--	--	9.31	--	--	--	--	--	--	8.89
Cu	7.60	9.11	7.71 9.52	--	--	--	9.84	--	8.55	9.44	--	9.08
Cd	10.10	10.16	12.25	11.79	12.14	--	--	--	--	--	12.84	11.23
Ca	3.00	3.02	5.32 4.72	--	5.01	7.59	9.66	9.04	7.37	10.25	6.70	7.29
Mg	2.80	2.81	4.91 4.51	--	4.70	6.68	9.25	8.33	--	7.95	--	--
Na	2.30	2.30	6.26	--	5.75	--	--	--	--	--	--	--
K	3.50	3.50	--	--	6.54	--	--	--	--	--	--	--
H	--	8.00	2.97 4.73	--	9.95	--	5.54	7.83 8.57	5.00	7.06	8.74	--

Notes:

1. Numbers in the matrix are negative logarithms of concentrations. To simplify the table all Cd complex concentrations below 10^{-13} M and all other complex concentrations below 10^{-10}M were omitted.

2. SAL, GLY, and PHTH stand for salycilate, glycinate, and phthalate, respectively.

3. When more than one number appears in the complex matrix more than one complex was important. (See Note 1.) There were two Cu^{2+} - CO_3^{2-} complexes, $CuCO_3^0$ 7.71 and $Cu(CO_3)_2^{2-}$ 9.52. All other double entires show increasing protonation of the ligand. (e.g. $CaCO_3^0$ 5.32 and $CaHCO_3^+$ 4.72.)