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THE TRACE ELEMENT GEOCHEMISTRY OF  
MARINE BIOGENIC PARTICULATE MATTER

by

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ROBERT WILLIAM COLLIER

Submitted to the Joint Oceanographic Committee of the Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, and the Woods Hole Oceanographic Institution on November 25, 1980, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Plankton samples have been carefully collected from a variety of marine environments under the rigorous conditions necessary to prevent contamination for major and trace-chemical analysis. Immediately after collection, the samples were subjected to a series of physical and chemical leaching-decomposition experiments designed to identify the major and trace element composition of particulate carrier phases. Elements examined through some or all of these experiments were: C, N, P, Mg, Ca, Si, Fe, Mn, Ni, Cu, Cd, Al, Ba, and Zn. Emphasis was placed on the identification of trace element/major element ratios in the biogenic materials.

The majority of the trace elements in the samples were directly associated with the non-skeletal organic phases of the plankton. These associations included a very labile fraction which was rapidly released into seawater and a more refractory fraction which involved specific metal-organic binding. Calcium carbonate and opal were not significant carriers for any of the trace elements studied. A refractory phase containing Al and Fe in terrigenous ratios was present in all samples, even from the more remote marine locations. The concentration of this carrier phase within the plankton samples varied in proportion to the estimated rate of supply of terrigenous matter and in opposition to the rate of production of the biogenic particulate matter. The aluminosilicates contributed insignificant amounts to the other trace elements studied. A trace concentration of particulate Al was identified which was more labile and associated with the organic fractions of the samples.

Variations in the surface water concentrations of dissolved Cu, Ni, Cd, and Zn with respect to P are compared to the ratios measured in the plankton samples and their regeneration products. The trace element/major element ratios in the residual plankton materials can be combined with estimates of the carrier fluxes to account for the

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transport of trace elements required to maintain their deep enrichment.

A variety of processes determining the geochemical cycles of specific trace elements were identified. As much as 50% of the Cd, Ni, Mn, and P are rapidly released from plankton and recycled within the surface ocean. During this process, the metal/P ratio in the residual particles must decrease by 10-30% for Cd and increase by a factor of 2-4 for Ni and Cu to balance their deep enrichments. Although Mn is taken up and regenerated by plankton, the magnitude of this process is small with respect to other non-biogenic Mn fluxes and has very little influence on its dissolved distribution. The Ba content of all known surface carriers is insufficient to account for the deep enrichment of Ba. A secondary concentration process results in the formation of significant particulate Ba within the upper thermocline.

THESIS SUPERVISOR: Professor John M. Edmond, M.I.T.

DEDICATION

To Pat and my parents

### ACKNOWLEDGEMENTS

I am grateful and deeply indebted to John Edmond for years of active support, guidance, and friendship that has made this research possible and fruitful. Ed Boyle has shared his insight and experience in trace element chemistry and so much more over the years we have known each other. Michael Bacon and Peter Brewer have also advised me in this research and in the preparation of this thesis. I thank them for their patient confidence. James Morgan and Francois Morel gave me helpful advice and support in my education and research. Research and discussions with James Bishop helped to initiate and guide my work on the chemistry of biogenic particulate matter in the oceans. I have been dependent on the inexhaustible energy and assistance given me by Barry Grant and thank him for making so much of my work successful. The captains and crews of numerous research vessels helped me collect my samples. Darlene Ketten patiently assisted in the identification of the organisms collected in this research. Bob Stallard was a friend through our many years of coexistence as students.

It is impossible to separate the importance of scientific exchanges from the friendship offered by all of these people. I especially thank Russ McDuff for his close friendship and life-saving support over the past few years. Mike Thomas and John Rueter have been, and will always be valuable friends.

There are many, many other fellow students and workers that have helped me along the way. I could not possibly name them all here. Quoting one of them - "They know who they are, and so do I."

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It is insufficient to merely thank my mother, father, and family for all they have given and have meant to me through these years. I love them for all of this and more.

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Chapter I

Introduction

## I. INTRODUCTION

The marine geochemistry of trace elements has been a primary focus of oceanographic research activities for the past decade. With the development of improved sampling and analytical techniques it has been demonstrated that many of the trace elements show large concentration variations in both vertical profile and areal distribution. Because of this heterogeneity, these elements are extremely sensitive tracers of physical, geochemical, and biological processes in the oceans. The vertical and horizontal segregation of the trace elements often parallels that of the major nutrient elements involved in organic cycles. These gradients are driven by the production, transport, and remineralization of particulate organic matter. Most of the recent research on the biogeochemistry of trace elements has focused on the "fingerprints" left by these biological processes in the water column and in the sedimentary record.

The trace elements Cd and Zn have dissolved distributions which closely follow those of  $PO_4$  and Si, respectively (Boyle et al., 1976; Bruland, 1980). These metals and nutrients are depleted in surface waters to concentrations which are less than 1% of their deep Pacific values. Cd is regenerated rapidly such that it correlates linearly with  $PO_4$  in the water column. Zn is regenerated more slowly and has a deep distribution which is similar to that driven by the production and dissolution of opal and  $CaCO_3$ . Another group of trace elements, represented by Cu, Ni, and Ba, also show deep enrichments - but to a much smaller degree (Chan et al, 1976; Boyle et al, 1977; Bruland, 1980).

Their surface water concentrations are never depleted below 10% of their deep concentrations and their correlation with the nutrients show significant complexity - especially near the surface and sediment interfaces. Other trace element distributions, including those of Mn and Al, show little relationship to the nutrient cycles (Klinkhammer and Bender, 1980; Hydes, 1979). In order to better understand the variety of processes controlling the distribution of the trace elements, the specific biogenic components must be independently determined. The intention of this research is to quantify the magnitude of these biological cycles by direct examination of the major and minor element compositions of plankton and their remineralization products.

Marine sediments also reflect the character and magnitude of biological activity in the surface waters above them. They are complex mixtures of refractory biogenic materials, lithogenous particles, and hydrogenous phases. Systematic attempts have been made to separate the end-members contributing to the sedimentary record by factor analysis (Heath and Dymond, 1977, 1980; Dymond, 1980), but the results of these models are sensitive to the assumed compositions of the end-members. Direct examination of biogenic particulate matter is necessary to quantify that component's contribution to the accumulation of each element in the sediments.

Biogenic Particulate Trace Elements.

Nearly all published chemical analyses of plankton and other marine particulate matter have been determined on bulk samples. Most include only the major or minor element composition of the sample - rarely both. Very few of the investigations demonstrated that the elements were quantitatively recovered and not contaminated during sampling or analysis. Experience gained in the collection and analysis of water samples for dissolved trace elements suggests that it is very likely that many of the reported plankton analyses are seriously contaminated. This fact, combined with other sampling and analytical problems discussed in this work, gives very little confidence in using currently reported plankton analyses in trace element geochemical models. Notable exceptions include analyses by Martin and Knauer(1973) who made serious attempts to address the problems of contamination in their samples. Martin et al.(1976) have also published the only set of quality analyses which include major components (P, Si, Ca) along with the trace analyses on the bulk samples.

There is a large body of data and a relatively detailed understanding of the processes controlling the fluxes of major biologically cycled elements. The intention of this research is to understand and quantify the trace element cycles by the extension of these major element cycles. This will be accomplished through the careful examination of the ratios and chemical relationships between the trace elements and major elements representing biogenic carrier phases.

The use of carrier models is not new in marine geochemistry. The extreme example of their application is in the estimation of rare-isotope fluxes by using the total element fluxes, normalized by the appropriate isotopic ratios and fractionation factors. The sediment-component factor analyses of Heath and Dymond(1977,1980) and Dymond(1980) represent more complex applications of carrier models. The composition of each end-member is measured or otherwise estimated. It is assumed that one chemical fraction or assemblage of elements can uniquely represent the mass of each end-member in the sample. A factor analysis is then performed to determine the optimum combination of end-members describing the total sediment composition. One of the goals of this research is to provide independent constraints on the composition and nature of the biogenic inputs to the sediments so that the magnitude of other complex inputs can be determined.

Numerous carrier phases and types of associations are possible between trace elements and marine particulate matter. These include: terrigenous material scavenged by biogenic particles; specific biochemical functions associated with metabolic processes; inclusion within structural-skeletal materials such as  $\text{CaCO}_3$ , opal, or  $\text{SrSO}_4$ ; and scavenging processes at active surfaces such as hydrous metal-oxide precipitates. This research examines the significance of these carriers in open-ocean, surface plankton samples. The correlation between plankton compositions and the carrier ratios reflected in the water column and sediments will be linked to the known processes and fluxes determining the major element cycles.

The experiments performed in this research were not designed to examine specific trace element functions in the ecology of marine plankton. There is a serious need for quantitative estimates of the role of organisms in determining the distributions and fluxes of trace elements in the oceans and sediments. The complex biochemical and nutritional relationships between organisms and trace elements still need to be studied under simplified and controlled laboratory conditions; the geochemical problem is best approached through actual measurements in the field.

This research presents a comprehensive set of chemical analyses on a variety of plankton samples. These include the major element compositions as well as the concentrations of a group of trace elements. The specific trace elements were selected either because their dissolved distributions have been determined or because of some anticipated relationship to particulate carriers. Immediately after collection, the samples were split for total concentration determinations and were subjected to a series of chemical leaching experiments designed to separate carrier phases and associated trace elements. Two demands were imposed on the design of all experiments: the minimization of every possibility of trace element contamination and the prevention of avoidable dilution of the trace element signals in the leaching solutions. To satisfy the goal of relating the major and minor element cycles, within these necessary experimental constraints, numerous trade-offs were made between increasing the experimental complexity and decreasing the handling and splitting of the samples. Several other experimental strategies were developed.



Surface plankton samples were collected from open-ocean environments. Because the samples contained mixtures of phytoplankton and zooplankton, they should represent the average composition of the complex assemblage of particulate material that is produced, recycled, and transported out of the surface oceans.

From the moment the plankton sample was removed from the water, it was isolated in a non-contaminating environment. Every solution which came in contact with the sample, including the original seawater in which the sample was suspended, was quantitatively collected and analyzed to carefully maintain a check on the mass balance throughout the leaching procedure.

To eliminate, as much as possible, the complication of significant terrigenous material being included within the samples, sites were chosen for their relative remoteness from obvious sources of this end-member. Because of a need to collect at least several grams of plankton, the sites could not include the more oligotrophic regions of the ocean. The requirements of relatively productive and non-coastal environments led to a group of plankton tows collected from an Antarctic Circumpolar Current transect, the eastern equatorial Pacific, and the central equatorial and northern Pacific Ocean. Details of the hydrography, dissolved trace element profiles, sediment distributions, and plankton tows at each site are outlined in Appendix 1.

Chapter II

Experimental Methods

## II. EXPERIMENTAL METHODS

Over the past five years there has been a rapid expansion of interest in trace element geochemistry. Along with this there has developed an increasing awareness of the problems of sample contamination during collection, handling, and analysis. Many of these problems have been exhaustively detailed in recent publications of high-quality trace element analyses, and I will not retrace those developments here (Boyle, 1976; Boyle et al, 1977b; Schaule and Patterson, 1978; Klinkhammer and Bender, 1980; Bruland, 1980). Specific details which are unique or important to this research will be covered, but it should be noted that every step in the preparation, collection, storage, and analysis of these samples has been executed with "continuous contamination consciousness".

### Seawater Samples

Seawater samples used in this research include hand collected surface samples and Niskin hydrocast subsamples. The surface samples were collected in two ways: from the main research vessel and from a non-metallic raft positioned well away from the ship. In the first procedure, water was collected directly into a hot-acid-leached linear-polyethylene storage bottle mounted on an all-plastic holder and lowered on a polypropylene line from the bow of a forward-moving vessel. The second procedure involved the filling of the storage bottle by hand from a Zodiac rubber raft located at least several hundred meters upwind (upstream) of the main research vessel. The Niskin casts from

the Galapagos and MANOP cruises were taken with new, carefully cleaned, 30-liter Niskin bottles with silicon rubber O-rings and new PVC-coated internal springs or external butterfly-valve closures (O.S.U. design).

Upon return to the ship's laboratory, the samples were moved to a filtered-air laminar-flow work station, acidified to pH 2 with vycor-distilled 6N HCl, and stored until analysis. Thus the trace metals determined represent the total dissolvable fraction.

All nutrient concentrations were determined by standard analytical techniques outlined in Riley(1975). Specifically, on the Antarctic and MANOP samples, the  $PO_4$ ,  $NO_3$ , and Si were determined colorimetrically using modifications of methods of Murphy and Riley(1962), Gardner et al(1976), and Mullin and Riley(1955). The nutrient chemistry at the Galapagos site was determined by colorimetric methods on a Technicon AutoAnalyser.

Determinations for Cu, Ni, and Cd were carried out by a modification of the method of Boyle et al.(1980). The metals were coprecipitated with cobalt-pyrollidine dithiocarbamate from 35ml of seawater in teflon centrifuge tubes. The precipitates were spun down, washed, digested with 6N  $HNO_3$ , and redissolved in 0.1N  $HNO_3$ . Each sample was completely processed in a laminar-flow work station within a single centrifuge tube, thus minimizing handling, transfers, and exposure to contamination. The concentrated solutions were then analyzed by flameless AAS with recoveries determined by standard additions and cobalt analyses.

### Plankton samples

Collection of uncontaminated particulate matter samples at sea is one of the most demanding sampling tasks. No method has been devised that will provide both freedom from contamination and large quantities of sample, and certain compromises have to be made. The generally low concentrations of plankton in open ocean surface water and the trace concentrations of the elements studied make it necessary to sample all of the particulate matter within a very large volume of water. This takes a fairly long time, throughout which the sample is exposed to contamination. Therefore, the water towed through must never have been in contact with any significant source of contamination (i.e., the sampler or the research vessel.) All towing equipment must be constructed of non-contaminating materials, and its handling must be equivalent to that demanded by other trace-element procedures.

Throughout this research, one set of identical plankton nets was used (Fig. II-1a). These were conical, 3:1 in length-to-width ratio, with a 0.5 meter mouth, and made of 44 $\mu$ m Nitex nylon. The plankton were concentrated into two in-line, 1000 and 44 $\mu$ m Nitex bags contained in a PVC cod end, which was tied into the end of the net with a nylon cord (Fig. II-1b). The mouth ring was epoxy-coated brass and was sewn completely inside of the leading seam of the net. The net harness and all fittings were of nylon and were eye-spliced around the net mouth ring. The tow line was polypropylene taken up on a PVC drum through nylon and PVC blocks and rigging. A 2-gallon polyethylene jug with handle was filled with scrap lead, tightly closed and sealed in plastic, and used on the end of a polypropylene line as a towing weight.

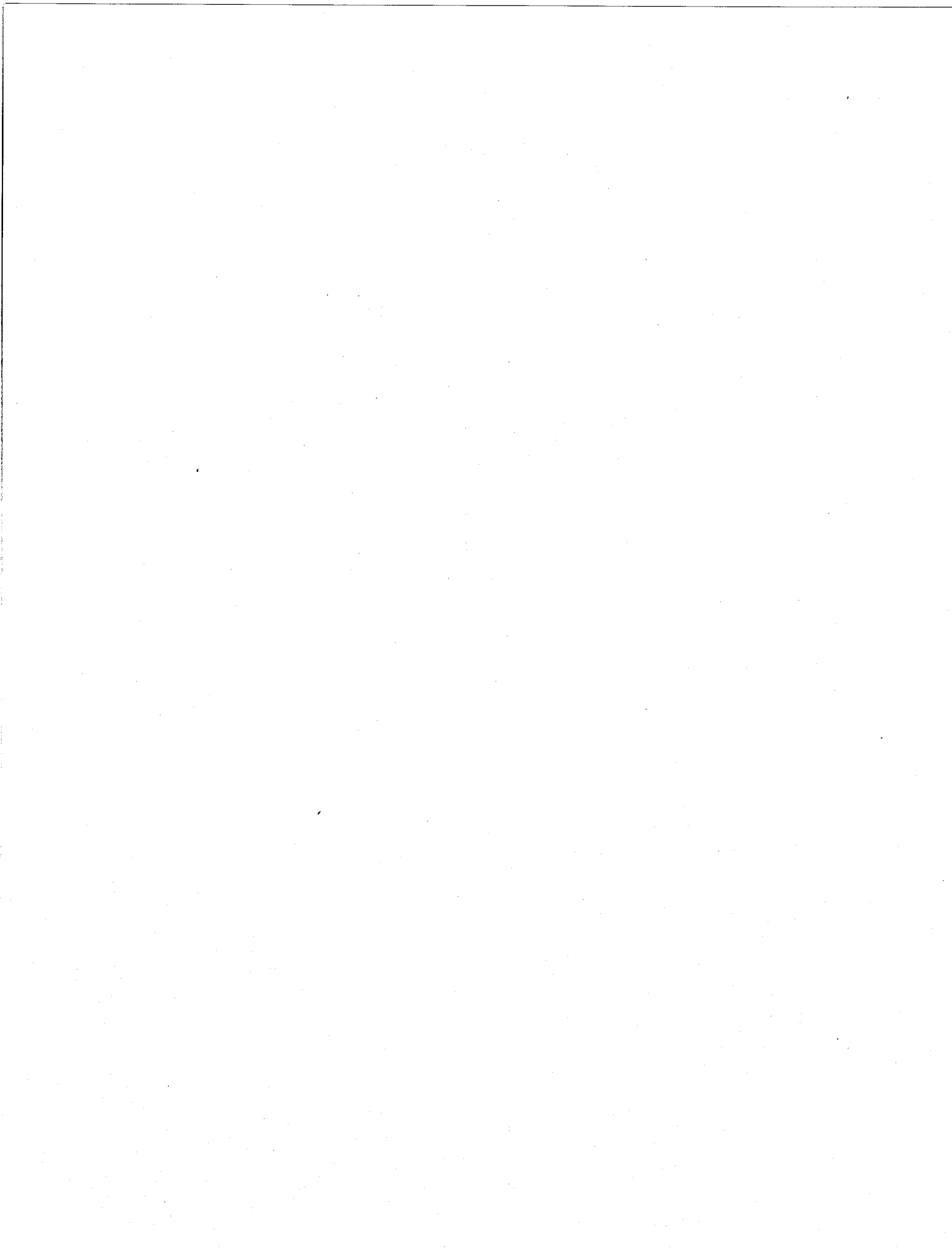
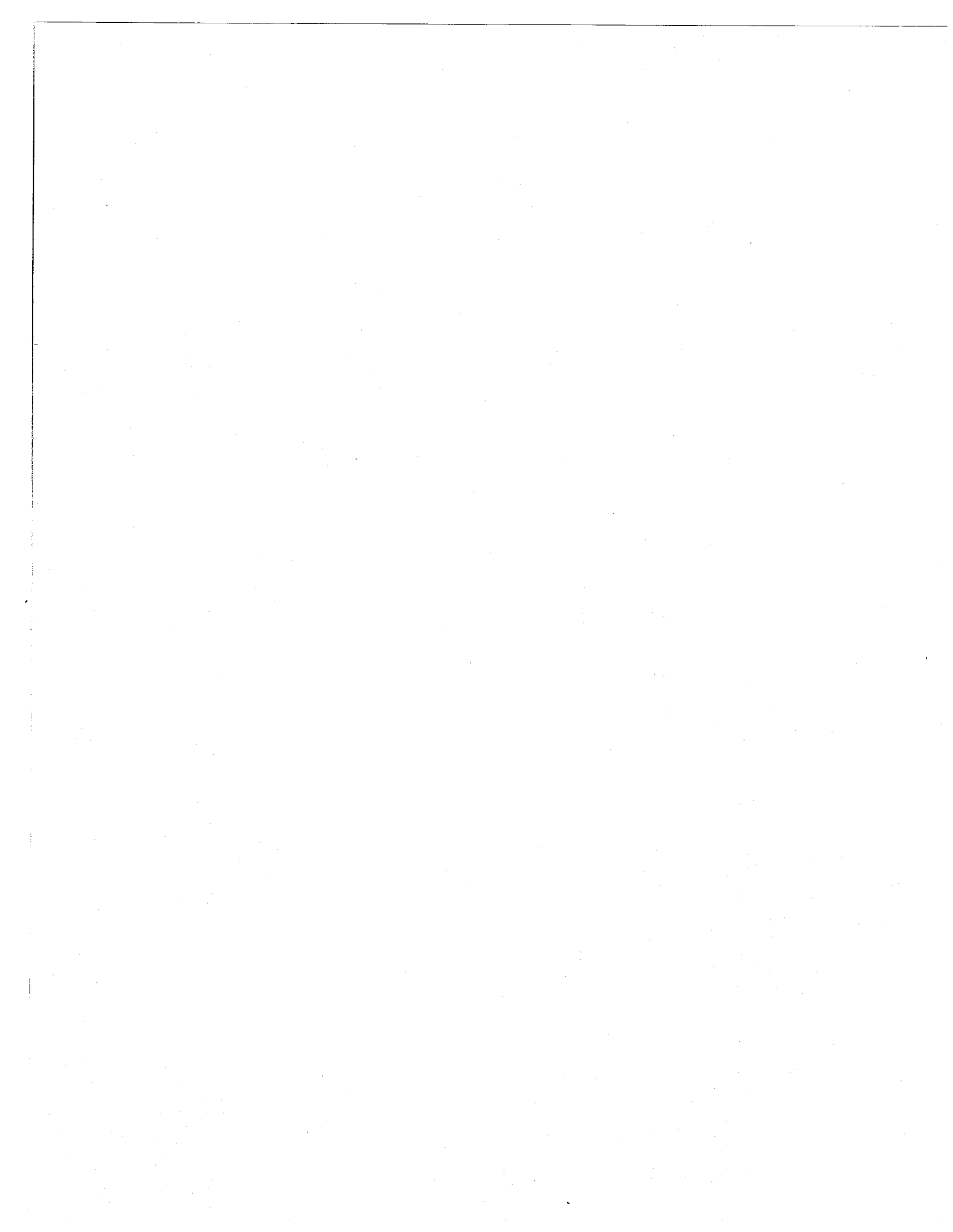


Figure II-1. Plankton sampling equipment.

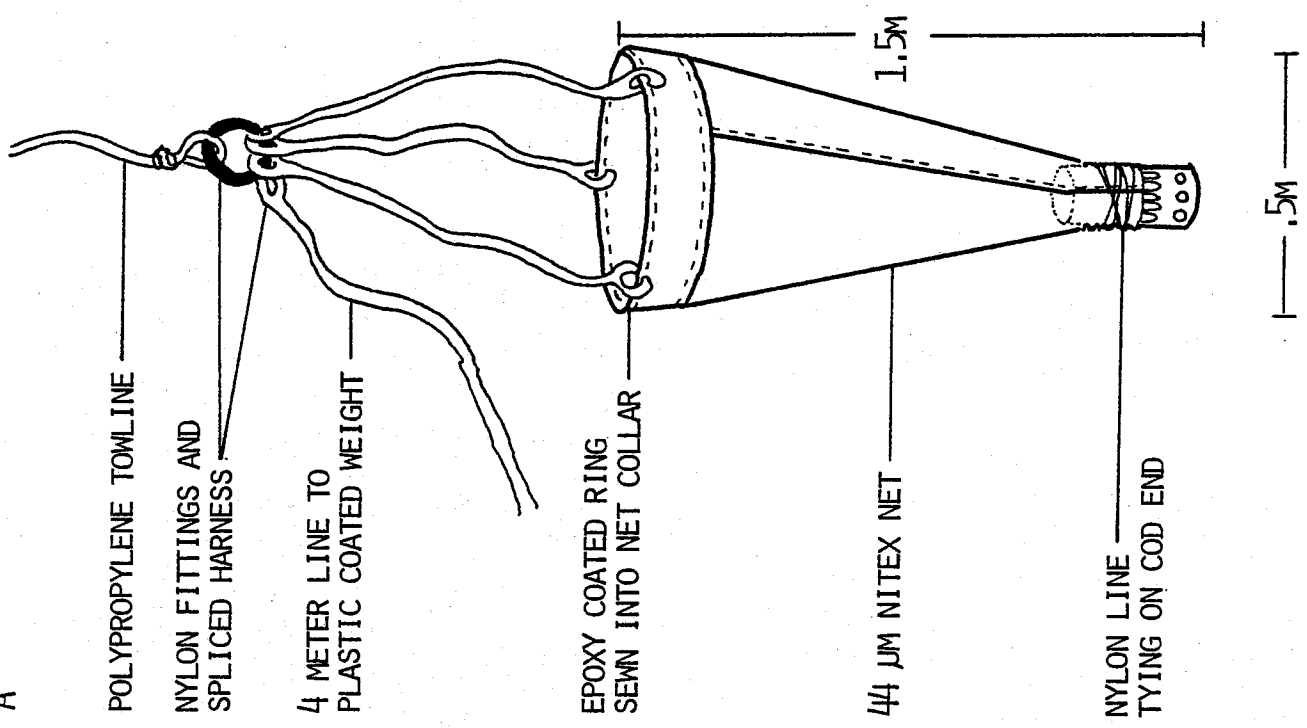
A) Net.

B) Cod end.

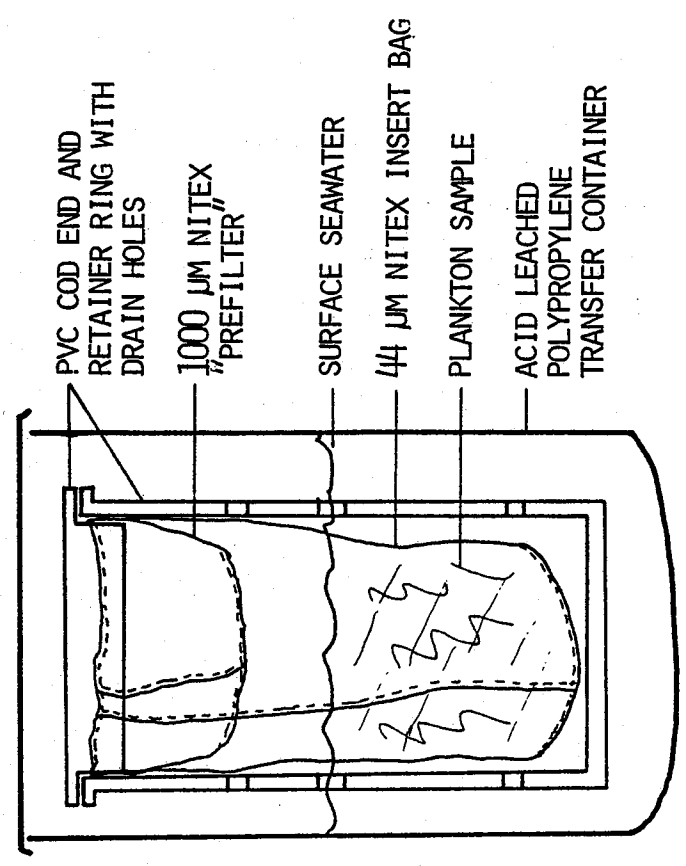




A



B



The net and towline were carefully cleaned before going to sea and were further cleaned before and after each use on station by towing through the surface seawater without the cod end installed.

Three basic towing configurations were used. Most samples (all Galapagos and most MANOP) were collected by manual vertical tows from an inflated rubber raft (Zodiac), which was moved at least several hundred meters away from the main research vessel. A small motor was used to get away from the ship but was removed and stored before any of the towing equipment was set up (Fig. II-2a). The complete tow was accomplished while drifting well upwind (upstream) of the ship. The net and weight were allowed to free-fall to approximately the base of the mixed layer (40-75 meters at these sites). They were then raised as rapidly as possible with the PVC winch to within 5 meters of the surface, then immediately dropped back down. This raising and lowering procedure was continued until enough sample had been collected - usually 2 to 3 hours, 30-50 lowerings - or until the operators had "expired". The procedure sampled a maximum of about 400 m<sup>3</sup> of seawater (not accounting for net clogging) and provided a sample of two to ten grams dry weight from productive surface waters.

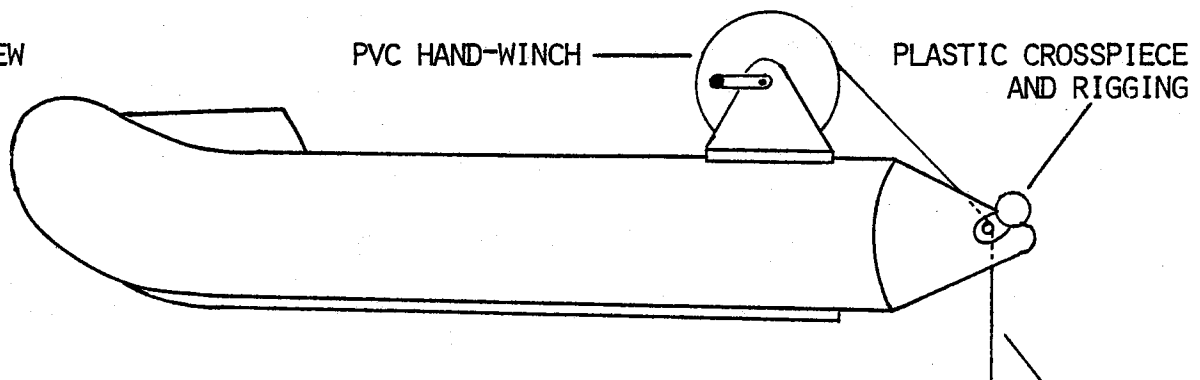
The hand-towing method, although far superior to normal ship tows in preventing contamination, was severely limited by wind, sea-state, and the low concentration of plankton found in the surface waters of oligotrophic environments. Therefore some plankton tows were collected from the main research vessel. The utmost care was used in setting up a system that would minimize the likelihood of contamination. In the Antarctic and at two of the MANOP stations the towing rig used in the

Figure II-2. Plankton towing rigs and procedures.

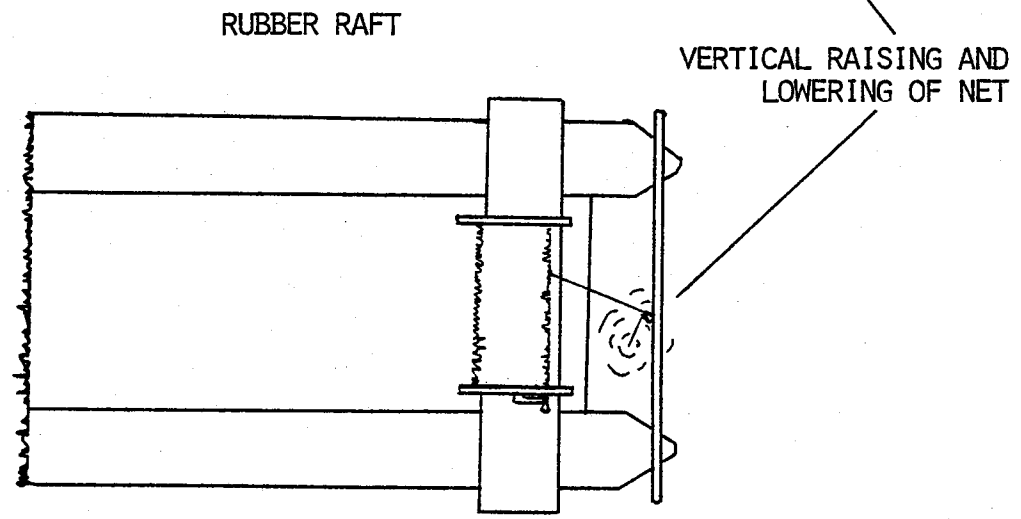
A) Zodiac rigging.

B) Ship and boom rigging.

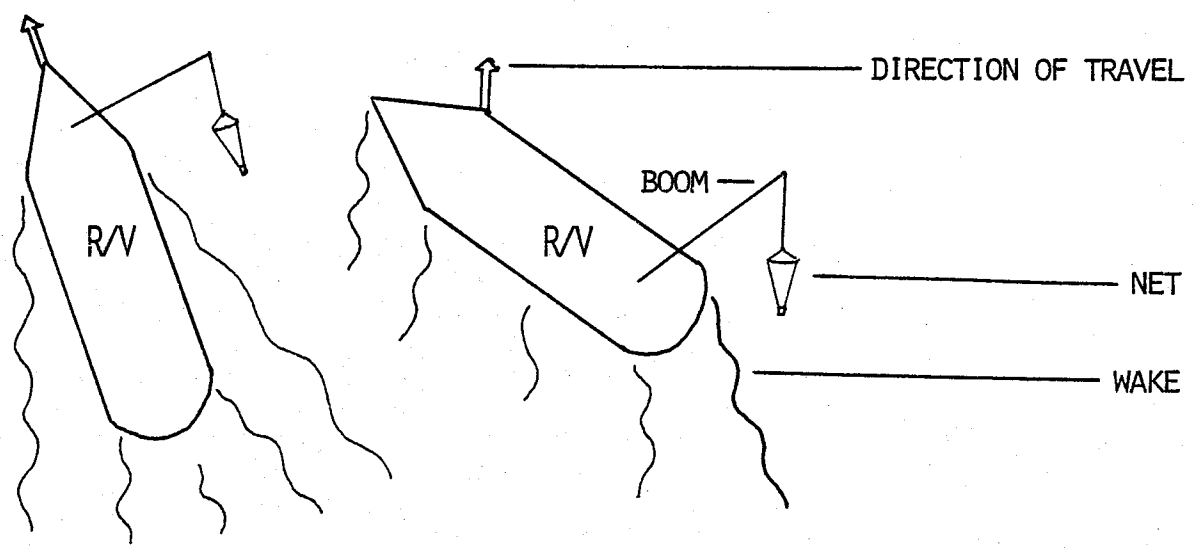
SIDE VIEW



TOP VIEW



B



Zodiac was set up using a long boom which extended away from the ship over waters which were undisturbed by the ship in its direction of travel (Fig. II-2b). Airborne contamination within the ship's environment can also be severe (Ferguson et al, 1970) so the net was carefully protected before and after each deployment. The tows from the ship were done at 2 knots for 30 to 75 minutes at a depth of about 5 meters with a much heavier weight to limit aft-trailing of the net. The maximum volume of water sampled was  $700 \text{ m}^3$  per hour at this towing speed. In the case where a comparison could be made between the Zodiac and ship tow (MANOP S, tows 3 and 6, Table III-4) the elemental compositions of the two materials from the same site gave no indication of any contamination due to the ship. The Antarctic tows were collected from the main research vessel and represent some of the lowest total metal concentrations ever reported for plankton (Table III-4). This further supports the integrity of samples collected in this manner.

The cod end was cleaned before each use and loaded into a polyethylene container in the laminar flow hood. Immediately before deployment, the cup was carefully tied into the cleaned net. At the end of the tow, as the net was brought to the surface, it was closed off and the cod end was untied and placed in the polypropylene container with clean, freshly sampled surface seawater. The sample container was kept cool in iced water until return to the ship for processing. There the sample was transferred from the Nitex cod-end liner to a wide-mouth polyethylene bottle in the hood and stored for short periods of time in a dark refrigerator as sample splitting and

experiments were carried out. Processing was begun as soon after collection as possible. A subsample was taken and preserved in buffered 7% formaldehyde for microscopic examinations. These formalin-preserved samples and some dried filter material were examined by D. Ketten at MIT using a Zeiss Ultraphot II light microscope to estimate the types and relative numbers and volumes of various organisms in each sample.

#### Sample splitting

An important step in these experiments was the subsampling of the 1-5 gram plankton-seawater suspension. Plankton splitters were considered, and a rotating, quartered cylinder splitter was constructed out of lucite (Honjo, 1978). It was found, however, that the plankton samples were too small for efficient use of this splitter, especially on a rolling ship. Also, too much handling and washing with seawater were required to effect quantitative transfer. The plankton-seawater suspension was rendered as homogeneous as possible by a swirling agitation and then subsampled in 5 ml aliquots with an automatic pipet using wide, straight-sided, cylindrical polyethylene tips. Replicate analyses indicated that this method of splitting was sufficiently precise (+10%) when compared to the precision of the rest of the analyses.

Filter samples and Leaching experiments

For each net tow, a set of splits was immediately collected to represent the total untreated plankton composition. These subsamples were collected by filtration on 0.4 or 1.0 $\mu$ m Nuclepore filters or by centrifugation as detailed below. All filtrates and supernates were saved for analysis. The apparatus and procedures used for filtration and centrifugation are shown in Fig. II-3. The collected filters were not washed, so they contained some volume of the seawater that the plankton were suspended in. The filters were placed on a clean teflon sheet and dried at 60 degrees (C) under a filtered air environment.

Some of the centrifuged subsamples were saved for calculation of total concentrations. The rest were resuspended in leaching solutions designed to selectively solubilize the particulate samples. The specific reagents and solutions used in these leaches are listed in Table II-1 along with the purification procedures used to reduce contamination. The general procedure in the leaching-centrifugation experiments was as follows. The splits of the seawater-plankton suspension were placed directly into a series of 50 ml teflon centrifuge tubes with polyethylene caps and were spun down in an IEC clinical centrifuge at approximately 1700 rpm for 10 minutes. The supernate solution was carefully removed from the top of the sample using a cleaned vacuum aspiration device (Fig. II-3) which collected the solution directly in a clean storage bottle. The sample was then suspended in a leaching solution, carefully agitated for 5 minutes, and re-centrifuged for 5 minutes. The leaching solution was aspirated from the sample tube, and the leaching process was repeated a total of three

Figure II-3. Sample processing apparatus for filtration and centrifugation.



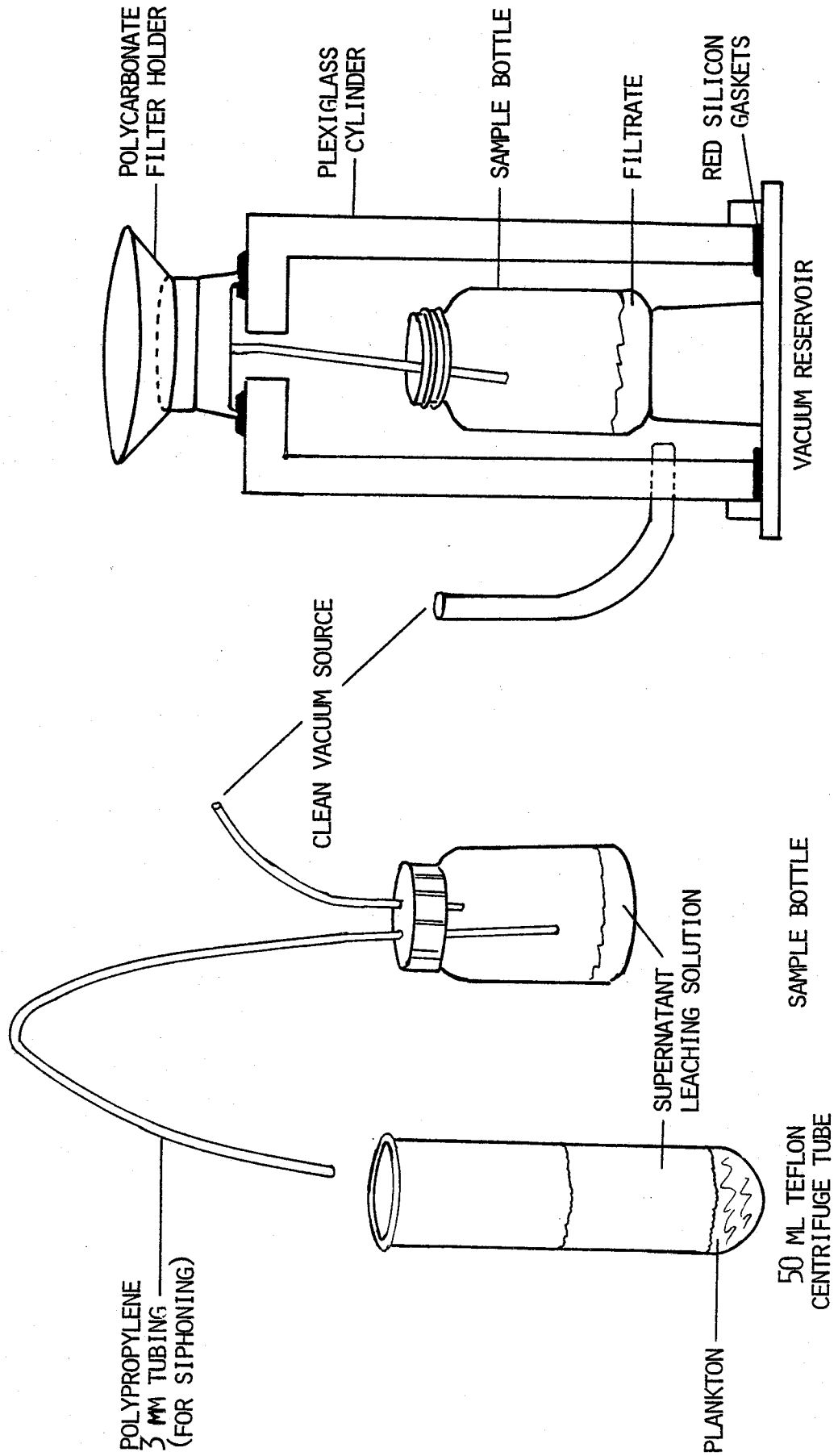


Table II-1. CHEMICAL REAGENTS USED IN LEACHING AND ANALYSIS

Solution or reagent	Notes
Surface Seawater	Hand collected at the time and site of the plankton tow. This water is analyzed for nutrients and trace elements and these values represent the blanks for further processing.
Distilled water	Distilled at MIT and transported to sea in polyethylene containers. Processing involves boiling distillation, deionization, followed by another quartz-glass distillation. Blanks are usually below detection and never significant to these analyses.
Ammonium chloride	Synthesized from 6N HCl (vycor distilled) which was bubbled with clean $\text{NH}_3$ to a pH of 5.5. The resulting solution was desiccated and the collected crystals dried at 105 degrees. Solutions were made 0.56N with distilled water (which is iso-osmotic with seawater-34.8%) and pH adjusted to 8 with $\text{NH}_3$ .
Ethanol, chloroform	Reagent grade solvents, redistilled 2X in vycor glass and stored in teflon.
HCl (6N)	Distilled 2X in vycor and checked for blanks.
$\text{HNO}_3$ (16N)	Reagent grade acid distilled 3X in vycor and checked for blanks.
HF	Baker Ultrex.
$\text{H}_2\text{O}_2$ (30%)	Baker Ultrex, blanks checked.
$\text{HClO}_4$ (70%)	GFS Co., 2X distilled from vycor glass.
APDC	Reagent grade prepared to 2% w/w in $\text{H}_2\text{O}$ . Solution purified by repeated extraction with chloroform.
EDTA	Aldrich Chemical, Gold Label, blanks checked.
Ascorbic acid	Grand Isl. Biol. Co., blanks checked.

times for each solution. The three supernates were generally combined to represent the total elements leached by a particular solution. A typical volume of leachate was 15 ml per step (total of 45 ml over three steps), and the carry-over of solution between centrifugation steps was approximately 2-3 ml. During the change to a new solution, better than 95% "purity" is attained by the second step and better than 99% by the third. The carried-over solution in the final mixture of the three supernate steps was on the order of 5% and was rarely a consideration in calculating the amount of an element which was associated with the particular leaching solution. Again, all procedures, except for the actual centrifugation of the sealed teflon tubes, were carried out in the filtered-air laminar-flow work station.

#### Total elemental concentrations and computation of mass balances

The total elemental concentrations in samples were computed in several ways. An assumption inherent to the sample splitting process is that the plankton mixture is basically homogeneous in composition with respect to the size fraction subsampled for analysis. The general validity of this assumption is born out by the consistency of replicate chemical analyses on different splits of one sample (Table III-6). Further, it is assumed that differences between the total measured mass of an element in two subsamples are more likely to be due to errors in the bulk mass transferred to each subsample than to sample heterogeneity. In this case, the ratios between the mass of each element in two different subsamples should be a constant. If subsampling were perfect, then this ratio would be equal to 1.

Filter subsamples served as the absolute indicators of plankton mass. The ratio of any subsample volume to the filter subsample volume was used to estimate the mass in that subsample. This gravimetric mass estimate was then modified in light of the mean total elemental mass ratios in the supposedly equivalent subsamples.

Total elemental concentrations based on filter subsamples were calculated as the sum of analyses on the digested filter material and the seawater suspension removed from the plankton by filtration. The ground filter material was itself subsampled for various chemical analyses so that these samples can be considered to have the highest likelihood of sampling error and contamination.

The particulate matter from the centrifuge tubes was transferred without subsampling to teflon bombs and digested without further handling. Total elemental concentrations in these samples were again calculated as the sum of the various fractions collected. Totals in the subsamples preserved without leaching were expressed as the sum of the seawater supernate plus plankton residue. Analyses of solutions from the longer leaching series were all totaled to give the total element mass balance for each tube.

#### Analysis of Particulate Matter and Leaches

All solutions and particulate materials were analyzed at MIT with strict care in handling to avoid contamination. The particulate samples were of two general types - filters and centrifuged residues. The filters were used for mass estimation, Si concentration determinations, and some of the total trace element determinations from

the Antarctic and Galapagos samples. Masses on the preweighed Nucleopore filters were determined on a Perkin Elmer model AD-2 electro-microbalance after drying at 60 deg. (C) and desiccation. Sodium analyses on the solubilized material were eventually applied to correct for the included mass of sea salt. The Antarctic and some of the Galapagos samples were removed from the filters and ground in a high purity alumina mortar and subsampled for analysis. The particulate materials collected in the teflon centrifuge tubes were left wet and removed in total with small amounts of distilled water to a teflon container for processing.

#### Solubilization

The solubilization of all particulate matter for trace-element and most major-element analysis involved oxidative dissolution with hot  $\text{HNO}_3$  followed by dissolution of the opal and silicate phases with HF. Because of the possibility of trace element loss due to volatilization at higher temperatures (Buckley and Cranston, 1971), all processing steps were done at temperatures below 120 degrees (C) and, when possible, in a closed system. The procedure involved the transfer of the particulate fraction from a centrifuge tube or filter split to a Parr Co. model 4745 acid digestion bomb with long-taper sealed teflon cups. Five ml of  $\text{HNO}_3$  was added and the samples were digested at 120 degrees (C) for 24 hours. A very small amount of acid migration out of the teflon bombs was occasionally noted but every blank run indicated no significant contamination. On a few occasions, the residual organic matter was further digested by a heating-evaporation cycle with more

HNO<sub>3</sub> and 100ul perchloric acid. The sample volume was reduced to near dryness on a hotplate and spiked with 0.5ml HF to dissolve the opal and any silicates which might have been present. After two successive spiking-volume reduction steps with 6N HCl to drive off the SiF<sub>6</sub>, the sample was taken up in 5 ml 0.5N HNO<sub>3</sub>. Table II-2 shows representative values of method blanks and recoveries for the bomb decomposition steps. On the basis of these results, all recoveries were taken to be 100% except for Al which was assumed to be 90%. The loss of Al was presumably due to the formation of some volatile Al-halogen compound. The most likely is AlCl<sub>3</sub> which sublimes near 180 degrees (C) at atmospheric pressure. Aluminum perchlorate also is volatile near this temperature, but AlF<sub>3</sub> should be stable to temperatures over 1000 degrees. The temperatures in the decomposition bombs should never have reached 180 degrees, but this is harder to control during the hotplate steps. The complex matrix in these samples also makes volatility estimates using pure-substance values uncertain. A value of 90% recovery will be taken for Al, with the realization that the loss due to this type of volatilization can be variable and dependent on the precise matrix and experimental conditions. The general agreement of replicate analyses on splits of the same sample support a relatively constant Al recovery.

Particulate samples to be analyzed for Si were leached in 0.4M NaCO<sub>3</sub> at 60 degrees for 5 days. After filtration and neutralization with HCl, the samples were analyzed for Si by the method of Mullin and Riley(1955). Particulate phosphorous analysis involved the digestion of samples in 0.5M potassium persulfate solutions followed by

Table II-2. Representative method blanks(A) and recoveries(B-%,(s))  
for acid-bomb particulate decompositions.

	Fe	Al	Zn	Ni	Cu	Mn	Cd	Ba
A)	1.0nm	0.4nm	0.1nm	0.1nm	75pm	25pm	5pm	<25pm
B)	101(5)	90(5)	99(1)	101(2)	97(1)	100(2)	101(1)	101(1)

colorimetric analysis of  $PO_4$  released to the solutions (Murphy and Riley, 1962). The  $PO_4$  was measured directly in the bomb decomposition solutions by the same technique.

Foraminifera from the Manop site S filters were hand-picked to collect approximately 2.5 mg of large individuals. These were suspended for 3 hours in a 50:50 mixture of 0.2N NaOH and 30%  $H_2O_2$ , heated to 60 degrees and ultrasonified occasionally. After washing in distilled water, they were subjected to a series of leaches designed to isolate the pure carbonate test and its included trace elements (Boyle, 1980). This involved the use of a basic reducing-complexing solution to remove any surface precipitated Fe or Mn hydroxide phases. After a 30-minute treatment with this solution at 90 degrees (C) with occasional ultrasonification, the forams were washed in hot and cold distilled water. The washing process caused the loss of about half of the mass of the forams through dissolution and mechanical loss but left a clean  $CaCO_3$  residue. The forams were then dissolved in distilled water under 1 atm.  $CO_2$  and the solution analyzed by flameless and flame atomic absorption spectrometry (AAS).

#### Major element components

Analyses of Na, K, Ca, and Mg were done by flame AAS using a Perkin Elmer model 403 spectrometer. Careful matrix matching, suppression of ionization and interference effects, and standardization by known additions were necessary to give good results in these varied and complex samples (Slavin, 1968). Carbon and nitrogen analyses on the dried splits of Galapagos sample filters were done at Woods Hole by



J.P. Clarner using a Perkin Elmer 240 CHN Analyser (Culmo,1969).

Methods for the analysis of phosphorous and silicon have already been discussed.

#### Analysis of Trace Elements

The trace elements in the solubilized plankton and leaching solutions were analyzed by atomic absorption spectrometry using electrothermal atomization. Two instrument systems were used: a Perkin Elmer 603 with an HGA 2100 graphite furnace; and a Perkin Elmer 5000 with an HGA 500 graphite furnace. These systems possess high dispersion monochromators , fast response peak-reading electronics, and give very good sensitivity. An effective continuum-source background correcting system in both the UV and visible spectrum was important for the direct analysis of elements in the presence of significant amounts of salt and organic materials. The graphite tube furnaces and their controllers offered a high degree of flexibility in determining the sample environment and heating program, and this was also very important in allowing analysis by direct injection. Model AS-1 autosamplers were used on both systems to improve the precision of each injection and allow a larger number of samples to be processed by multi-point standard additions in a single analysis run.

The wide variety of sample matrices encountered in this research required that analyses be made by a method using known additions of standards to the actual sample matrix (O'Haver,1976). The standard curve of absorbance vs standard spike concentration is used to give the concentration in the sample by extrapolation. Three very important

criteria must be satisfied to establish the validity of this method: 1) the linearity of the slope must be demonstrated throughout the measurement and extrapolation range of absorbances; 2) the absorbance of the blank matrix must be zero (or known); 3) there can be no unaccounted drift in sensitivity during the analysis of a single sample set. The simplicity of these requirements often leads to their being ignored and this can cause very severe errors during elemental analyses in complex matrices by flameless AAS. The need for standard additions and some of the difficulties encountered in their application to these samples can be seen by the following examples.

A solubilized filter sample from the Galapagos samples was analyzed for Cd two different times during a one year period (Table II-3). The identical instrument was used, and the only difference in the run was the sample dilution and the concentration of the standard additions. Increasing the sample dilution by a factor of 50 increased the relative sensitivity by a factor of 100 by removing the sea-salt chloride interference such that the absolute absorbance actually increased with increasing dilution! It is clear that the samples and standards must be perfectly matched in this type of situation.

The absorbance range over which the calibration relation is linear is generally much lower in flameless AAS than in most other common types of instrumental absorbance measurements. As a working procedure, the absolute absorbance of any peak used for analysis was always kept below 0.15 absorbance units (A). Experience has shown that above this value the calibration curve of several elements is nonlinear (Fig. II-4). The data for the iron calibration in Fig. II-4 show how the

Table II-3. Cadmium slope variations with dilution of salt matrix.

Sample- "vial 1" - 6 nm Cd/ml  
.1 mm Na/ml (0.2X seawater conc.)

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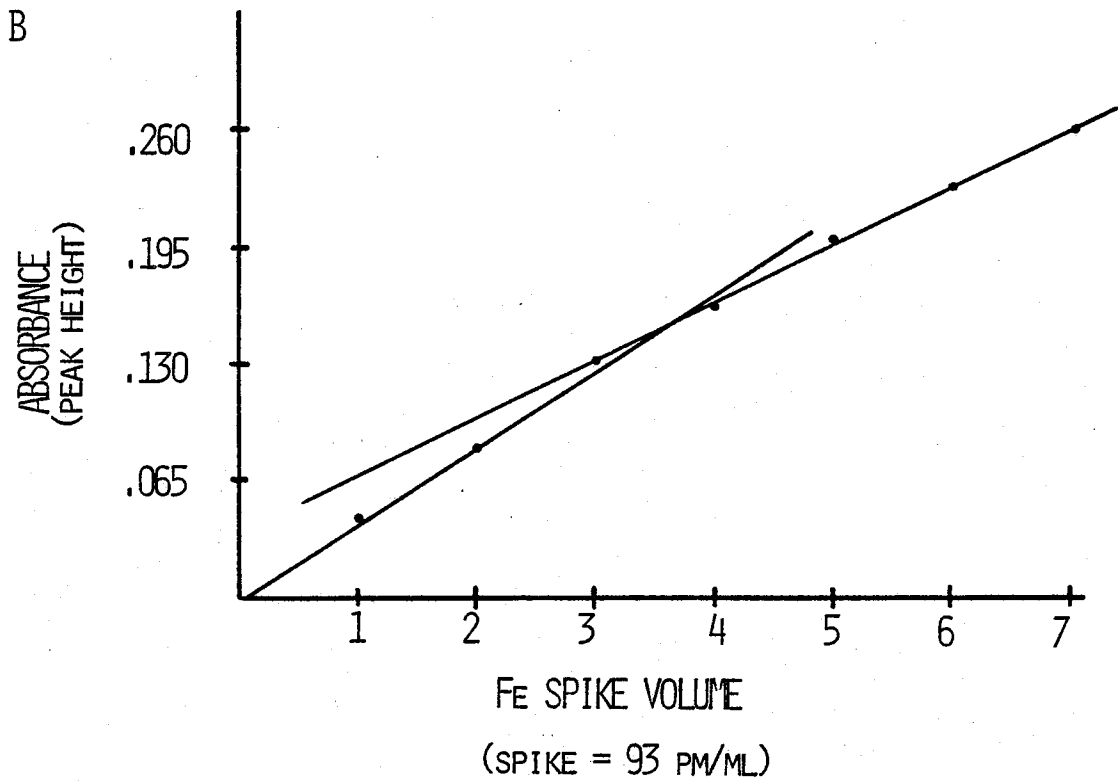
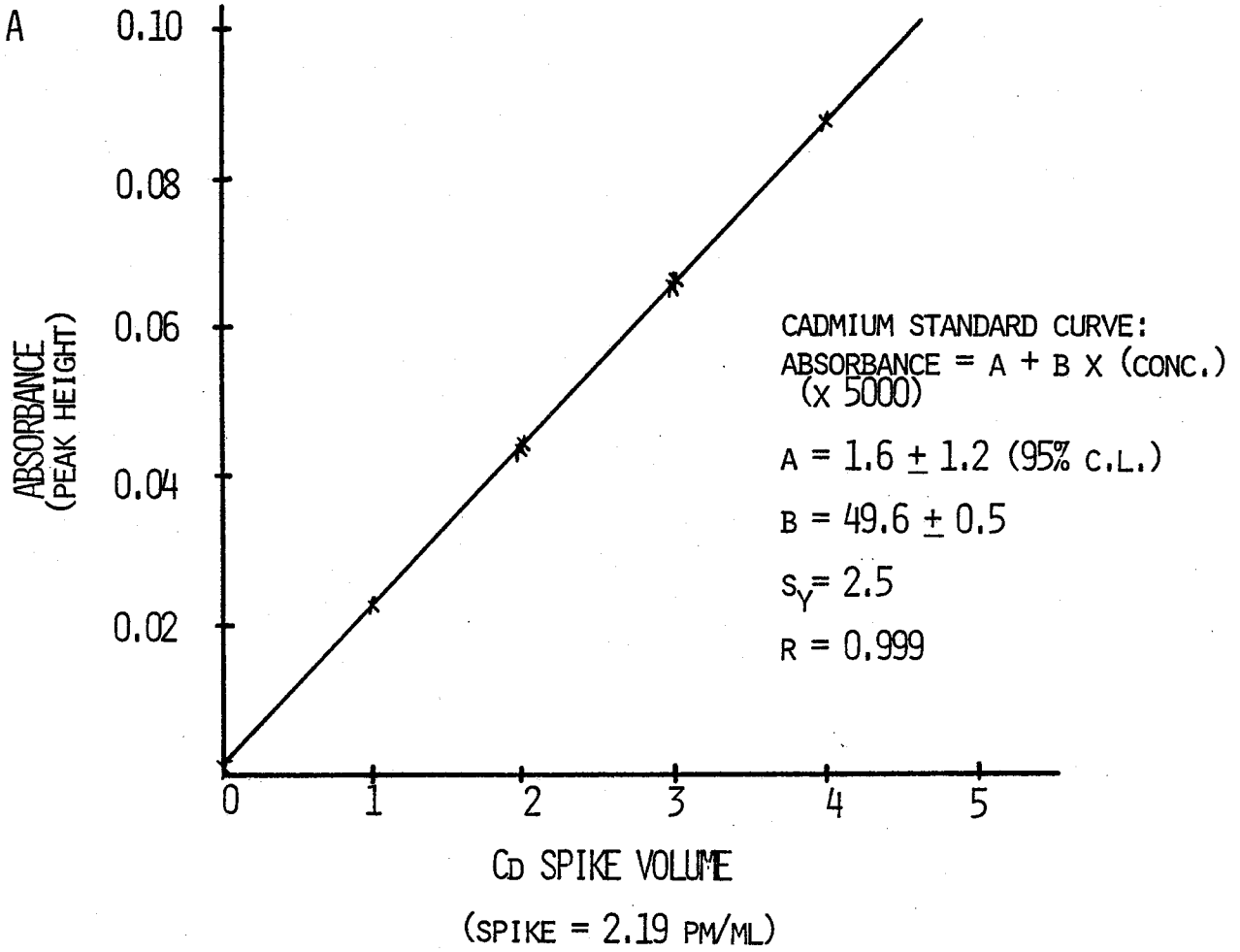
Analysis 1 - dilution X17.5  
slope  $5 \times 10^{-3}$  abs units/pm

Analysis 2 - dilution X846  
slope  $6 \times 10^{-1}$  abs units/pm

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increase in dilution ~ X50  
increase in sensitivity ~ X100

Figure II-4. Standard curves for Cd (A) and Fe (B).



relationship between added spike and absorbance in a three-point standard addition experiment could appear linear at a point well above that which could really be extrapolated to zero absorbance. This error would result in a predicted sample concentration which was much too high. The curvature seems to be more severe for elements requiring a small slit width to eliminate non-absorbing emission spectra of the AA lamps. This effect can sometimes be reduced by using even smaller slit widths. Again this behavior is shown in Fig. II-5 for iron and it has also been noted for cobalt and nickel.

The additive effects of any analyte blank or any non-specific absorbances or interferences must be known and compensated for. To truly assess the value of the blank in this method of standard additions, one must have a matrix-representative solution in which the concentration of the element of interest is otherwise known. For example, in the case of the seawater-plankton supernate solution, the concentrations of the elements of interest can be determined in a surface seawater sample by a preconcentration technique and these can be compared to the values determined by direct injection of an appropriately diluted sample of the same surface water. A typical behavior for non-element specific absorbances is shown in Fig. II-6. The timing of the maximum point in an analyte and an interfering peak will frequently be different. If they are sufficiently separated to distinguish them in a high-speed recording, then analysis is possible by graphically separating the analyte peak from the concentration-invariant background peak. Usually the sampling time of the peak-height reader can not be specified precisely enough to separate these,

Figure II-5. Effects of slit width on linearity of standard curves.

- A) Fe standard curves with .07 and .2 nanometer slits.
- B) Emission spectra of Fe hollow-cathode lamp.

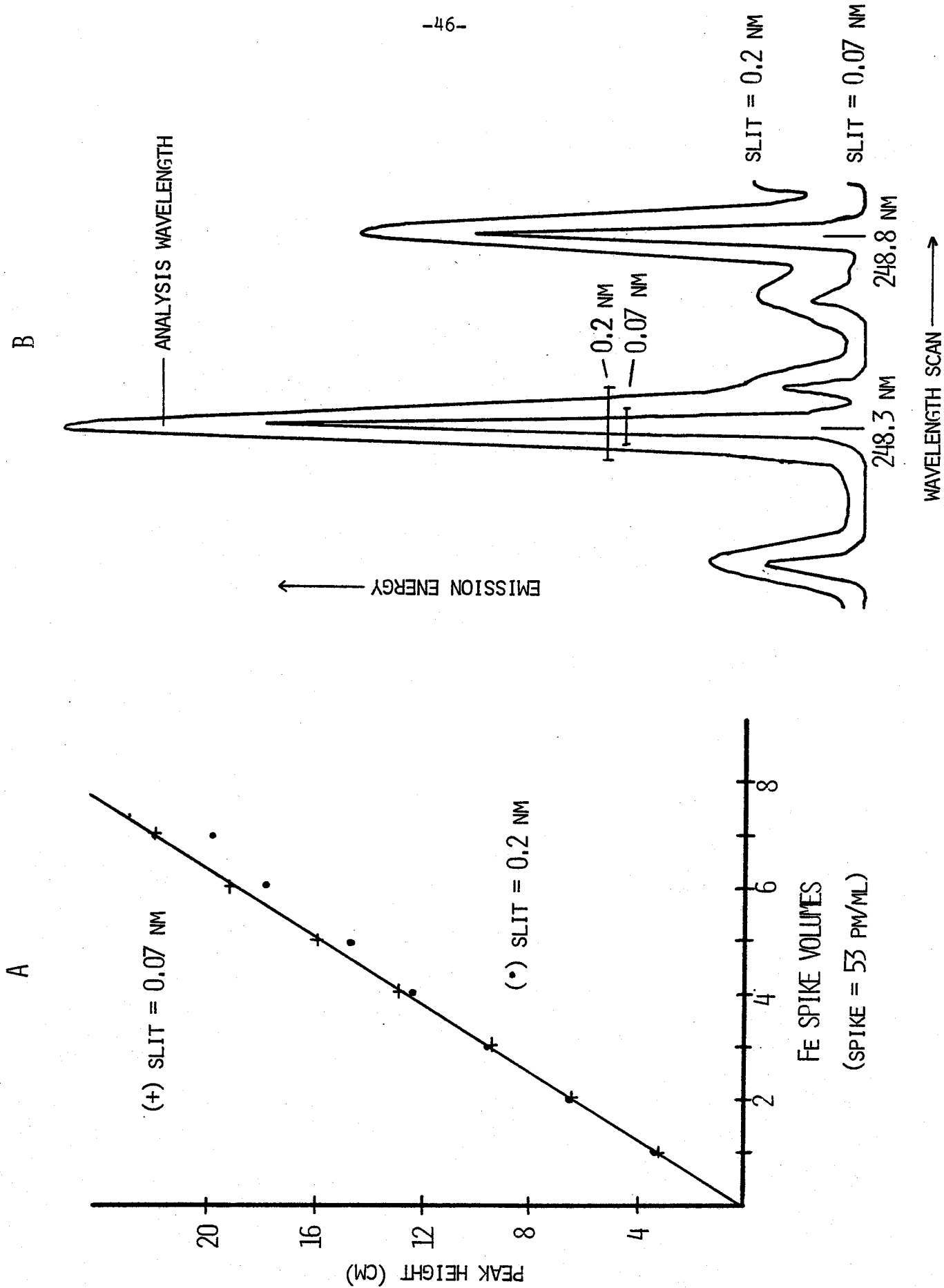
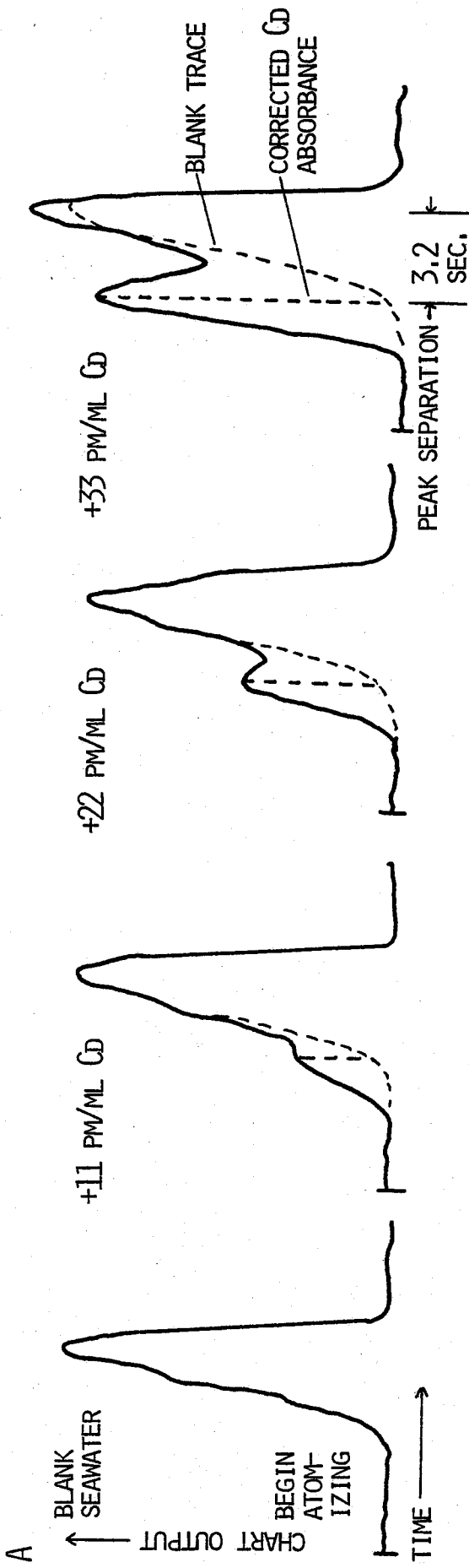




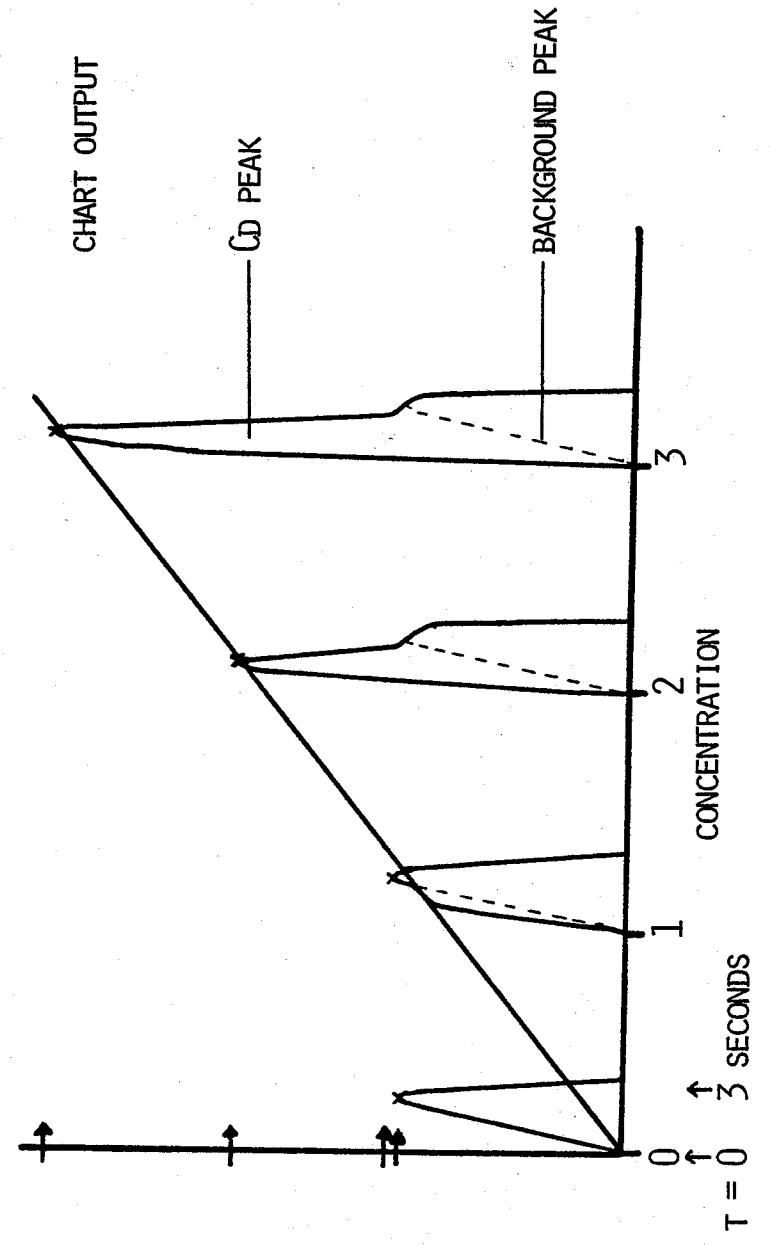
Figure II-6. Background absorbances in Cd determinations.

A) Expanded trace of absorbance vs. time.

B) Example of peak-reader output vs. concentration.



PEAK HEIGHT SEEN BY DIGITAL PEAK READER WITH 5 SECOND INTEGRATION TIME



and the maximum of the two peaks is picked up. The peak reader output does not change until the increasing analyte peak extends above the interfering peak. This results in a standard curve which "hooks" to a constant absorbance at very low concentrations. If sample and standard concentrations can be prepared to work above this low level then the known-addition extrapolation can still be made. Of course that is assuming that the upper, non-linear absorbance range has not been reached yet.

#### Matrix modification and matching

From the above discussion, it is clear that the precise duplication of matrix must be made in every sample and standard. Many of the elements form volatile chlorides as the precursor to reduction to the metal in the furnace (Sturgeon and Chakrabarti, 1978). In the presence of a great excess of chloride, the sensitivity is often reduced by the loss of the metal chloride from the furnace before reduction can occur. Incremental addition of a standard containing significant amounts of  $\text{HNO}_3$  to a sample containing HCl can change the sensitivity of the analysis. The addition of  $\text{HNO}_3$  presumably forces the evaporation of HCl and subsequent precipitation of metal nitrates, not chlorides in the graphite tube. Therefore, as far as possible, all additions to the sample were matched to balance dilution of the matrix and acid so that the only major variant was the analyte.

Another matrix modification used with samples containing high concentrations of dissolved materials (e.g., undiluted seawater samples) was the addition of ascorbic acid to the sample to arrive at a

final concentration of approximately 1% by weight ascorbic acid. Analyses of samples treated in this manner have much better reproducibility and higher sensitivities that approach those expected in non-salt matrices. The addition of organic acids has been investigated by numerous authors (Regan and Warren, 1978; Hydes, 1980), but the mechanisms of the effect are not well known. The ascorbic acid spreads the injected sample solution out over the inside of the graphite tube by changing the wetting properties of the mixture. This results in much smaller crystals of salt being formed on the surface of the tube after the sample is dried, allowing a more efficient and reproducible atomization of the sample.

#### Instrumental procedures

One of the critical steps in successful analysis of trace elements by flameless AAS in the presence of complicated matrices is the fine tuning of the graphite furnace operating program. This was accomplished by specifying a program of up to nine steps which was designed for the specific element and matrix. On the HGA-500, each step has digitally selectable temperature, heating rate, holding time, separate internal and external gas types and flows, and control of the peak reading-recording electronics of the spectrometer. Selective volatilization of solvents and salts and the oxidation of organic phases can significantly reduce major interferences. An annotated example program for the atomization of Cu from a 0.2N ammonium chloride solution is shown in Table II-4. Control of the heating rate, temperature, and internal gas flow before and during the atomization

Table II-4. HGA 500 graphite furnace program.

Analysis of Cu in 0.2N  $\text{NH}_4\text{Cl}$

Step#	Temp.	Ramp	Hold	Int. Gas	Comments
1	100	1sec.	0sec.	300cc/min	Jump to drying temp.
2	130	15	15	"	remove solvent w/o boiling.
3	160	15	15	"	remove hydration water
4	340	10	0	"	ramp to sublimation temp.
5	360	25	0	"	slowly sublime $\text{NH}_4\text{Cl}$
6	850	10	20	"	Char, also zero baseline.
7	2400	0	3	30	Atomize Cu, read abs. peak ht.
8	2600	1	4	300	cleaning step.
9	20	1	4	"	cool, look for baseline shifts.

step can be used to further separate the analyte appearance from that of an interfering peak. This can be applied to the example already mentioned for Cd (Fig. II-6). In the case of a salt interference, most of the salt is volatilized between 1500 and 2000 degrees. If the element being analyzed has an appearance temperature below this temperature (e.g., Cd) then it is possible to atomize it selectively, without the salt. If the element requires a higher atomization temperature (e.g., Ni) then a short (2-4 second) intermediate temperature step at 1600 degrees between charring and atomizing will start to remove the salt before significant amounts of the analyte are lost. Gas flows within the graphite tube can be varied to effect dilution and separation of two peaks when the appearance rate of the element is slow enough to be affected by a practical range of flow rates.

Graphite tubes used were of three types: normal unpyrolyzed tubes; tubes pyrolyzed at MIT; and batch-pyrolyzed tubes purchased from Perkin Elmer. For elements requiring a high atomization temperature, the pyrolyzed tubes always give more sensitivity by at least a factor of two. The Perkin Elmer pyrolyzed surface is usually the most sensitive available, but this sensitivity deteriorates rapidly, making the lab-pyrolyzed tubes the best choice for most elements except Ba, for which the P.E. tubes are necessary. The unpyrolyzed tubes are more porous and offer better reproducibility for low-temperature elements (Cd, Zn) and for some high-salt samples (Al). Again, compromises must be made between sensitivity, interference reduction, and precision.

Other important instrumental parameters include the careful overlapping of the background correction and hollow-cathode lamp image within the center of the graphite tube. The furnace must be perfectly centered in the light path to minimize the amount of stray emission picked up by the phototube. In essence, it is of the utmost importance that all instrumental parameters be carefully optimized under adverse sample matrix conditions.

Chapter III

Results



III-1. SHIPBOARD EXPERIMENTAL SUMMARIES

The experiments performed at sea on the plankton samples are described in Tables III-1, III-2, and III-3.

Plankton tows from three of the stations occupied on the Antarctic transect were subsampled onto filters and into centrifuge tubes for analysis (Table III-1).

Subsamples from the Galapagos tows (Table III-2) were collected on filters and in centrifuge tubes for several sets of leaching experiments. These included: isotonic ammonium chloride vs. distilled water; ethanol extraction; and a series of acid leaches. All particulate residues and leaching solutions were saved and analyzed.

The MANOP tows were collected from two sites and details of their processing are outlined in Table III-3. At site C, two tows were collected and split between filters and leaching experiments. The several sets of experiments performed included: isotonic ammonium chloride - distilled water leaching; filtration and ultrafiltration of the seawater supernate removed from the plankton suspension by centrifugation; an acid leaching series with long and short exposure times; an extraction with hot ethanol.

At site S, four tows were collected: two from the Zodiac and two from the boom-towed net. The amount of plankton collected in the Zodiac tows was so small that the number of experiments performed was severely limited. Only one filter subsample was collected and processed. The two leaching experiments were: resuspension of the centrifuged plankton in a millimolar EDTA - surface seawater solution

Table III-1. Antarctic shipboard chemistry summary.

- STN E - total concentrations only;  
filter A4 - 80mg  
ground and subsampled for analysis
- STN J1 - total concentrations only;  
filter A7 - 81mg  
ground and subsampled for analysis
- STN M - total concentrations and centrifuged leaching expts.  
filter A10 - 116mg  
ground and subsampled for analysis  
centrifuge tubes: 167mg each  
#3 - untreated  
#19 - initially untreated, H<sub>2</sub>O<sub>2</sub> washed before analysis  
#26 - distilled water, 0.1N HCl leached  
#22 - untreated, digested for Si analysis

(Unless otherwise noted, the numbers listed in Tables III-1,2,3 represent sample numbers for leaches, tubes, and filters.

The concentrations in each of these samples are tabulated in Appendix II in approximately the same order as presented in Tables III-1,2,3.)

Table III-2. Galapagos shipboard experimental summary.

TOW 1 - filters: GA200 - 97mg  
GA201 - 118mg  
centrifuge tubes: approximately 170mg each

Expt. 1 (8 hours after tow)

Tube #	91	92	98
Seawater centrate	<----	167	---->
NH <sub>4</sub> Cl	158	225	
Dist.H <sub>2</sub> O	160	226	

Expt. 2 (24 hours after tow)

Tube #	86
Seawater centrate	154
Dist.H <sub>2</sub> O	165
Ethanol (cold)	194

TOW 2 - no useful analyses

TOW 3 - filters: GA204 - 100mg  
GA205 - 73mg  
centrifuge tubes: approximately 160mg each

Expt. 1 (4 hours after tow)

Tube #	119	114
Seawater centrate	<--- 125 --->	
Dist. H <sub>2</sub> O	132	131
10 <sup>-3</sup> N HCl	149	130
0.1N HCl	135	118
HNO <sub>3</sub> -H <sub>2</sub> O <sub>2</sub>	<--- 129 --->	

Table III-3. Manop shipboard experimental summary

SITE C

TOW 1 - filters: GA217 - 99mg  
centrifuge tubes: approx. 200mg each

Expt. 1 (4 hours after tow)			
Tube #	T47	T48	T49
Seawater centrate	<-----	X186	----->
Dist. H <sub>2</sub> O	X197		
NH <sub>4</sub> Cl		X198	

Expt. 2 - Ultrafiltration of X186 (seawater centrate)  
filtrate collected in X177

TOW 2 - filters: GA220 - 42mg  
centrifuge tubes: approx. 71mg each

Expt. 1 (2 hours after tow)				
Tube #	T42	T43	T44	T45
Seawater centrate	X185	<-----	X188	----->
Dist. H <sub>2</sub> O		X184 (30min)	X175 (8hrs)	
10 <sup>-3</sup> N HCl		X189 (30min)	X172 (8hrs)	
0.1N HCl		X180 (30min)	X169 (8hrs)	
HNO <sub>3</sub>		x168 (2.5hrs)	X176 (24hrs)	
Ethanol (hot)				X178

Expt. 2 - filtration of seawater centrate X188

1.0µm nucleopore	0.4µm * nucleopore	0.1µm millipore VC	0.05µm millipore VM
X171	X183	X182	X163

\* - starting material for this sample was the original plankton suspension (not centrate) used in collecting filter GA220.

Table III-3. (cont.)

SITE S

TOW 3 - filters: GA222 - 22mg  
centrifuge tubes: approx. 71mg each

Expt. 1 (2 hours after tow)  
Tube # T37 T40

-----  
Seawater <-- X110 -->  
centrate

Surface X123 X117  
seawater w/EDTA w/o EDTA  
-----

TOW 4 - no material, net flipped over

TOW 5 - filters: none collected, no mass estimates made.

Expt. 1 (2 hours after tow)  
Tube # T34 T35

-----  
Seawater <-- X129 -->  
centrate

Surface X121 X128  
seawater w/oAPDC w/APDC  
-plus-  
Chloroform XT34 XT35  
-----

TOW 6 - filters: GA223 - 53mg  
GA224 - 31mg  
centrifuge tubes: approx. 133mg each

Expt. 1 - time release to seawater, cold, dark storage.  
Tube # T30 T29 T31 T32 T33

-----  
Seawater X127 X136 X125 X140 X76  
centrate (2.5hr) (12hr) (24hr) (72hr) (96hr)

TOW 7 - filters: GA225 - 92mg  
centrifuge tubes: approx. 230mg each

Expt. 1 - cold, dark, antibiotics.				Expt. 2 - warm, in light.		
Tube #	T1	T2	T3	T26	T28	T27
Seawater	X141	X137	X61	X139	X131	X109
centrate	(24hr)	(48hr)	(72hr)	(24hr)	(48hr)	(72hr)

and with a chloroform-APDC extraction mixture. Tows 6 and 7 were collected by the main research vessel and yielded much larger plankton samples. The particulate material was split into a series of centrifuge tubes to determine the rate of release of the various elements into the seawater in which the plankton were suspended. The first experiment separated the plankton from the seawater suspension at intervals over a 96 hour period. The samples were stored at 4 degrees (C) until the time of centrifugation. The second set of samples included the addition of an antibiotic mixture. The last set of samples was kept at surface seawater temperatures on the deck of the ship, exposed to sunlight.

The elemental compositions determined for each filter, centrifuged residue, and solution are tabulated in Appendix II. Unless otherwise noted, the values listed for the centrifuged subsamples and leaching solutions represent the total mass of elements in that particular sample. The concentrations for filters were determined on several weighed subsamples of the filters and combined on a weight-normalized basis.

III-2. TOTAL ELEMENTAL COMPOSITIONS

The total concentration of elements in the original plankton material must always be calculated from determinations on several fractions. In the simplest case, this involves the sum of concentrations in an untreated subsample of plankton and in the seawater that has been separated from the plankton. For other samples it involves summing the analyses on a series of leaching solutions and particulate residues. The concentrations determined in various subsamples from a single sample are combined and averaged to calculate an estimated total concentration for the tow. The calculated totals for all of the analyzed plankton tows are summarized in Tables III-4, III-5, and III-6. Details of the calculations involved will be briefly discussed.

Only filters and centrifuged particulates were analyzed from the Antarctic plankton tows. The values for stations E, J1, and M were based on analyses of filters A4, A7, and A10, respectively. Analyses of several centrifuged subsamples were used from site M. The total concentrations calculated represent minimum values since the calculations do not include the contribution of elements released to the seawater suspension. Judging from experience gained on other samples, it is expected that concentrations based on these particulate fractions are reasonable estimates for total Ca, Si, Cu, Fe, Zn, Al, and Ba. Estimates of P, Ni, Cd, and Mn may be low by a factor of two or three because of the rapid release of these elements from the plankton to the seawater suspension.

Table III-4. Total Concentration Estimates - All Stations

Estimates based on averages of subsamples of each tow. Samples used in the averages are summarized in Table III-5. The individual subsample estimates are given in Table III-6.

Concentration units (for Tables III-4,5,6):

Ca, P, Si, C, N	- mmole/gram dry plankton	
Fe, Zn, Al	- $\mu$ mole/gram	"
Cu, Ni, Cd, Mn, Ba	- nmole/gram	"

Values listed immediately below concentration are the standard deviation of the mean when more than one estimate was averaged from different subsamples. If no value is listed then the estimate is based on a determination on one subsample only.

(Table III-4 continued on next page)



Table III-4 (continued)

## Total Concentration Estimates All Stations

	ANTARCTIC			GALAPAGOS			MANOP C			MANOP S		
	STN M	STN J1	STN E	TOW 1	TOW 3	TOW 1	TOW 2	TOW 3	TOW 1	TOW 2	TOW 3	TOW 6
Ca	0.011	0.23	0.3	0.84 0.03	1.39 0.04	1.34 0.27	1.5 0.24	3.66 0.26	1.59			
F	0.024		0.22	0.42 0.04	0.35 0.02	0.26 0.03	0.3 0.01	0.44 0.01	0.36			
Si	12.3			1.28 0.01	0.68	0.56	0.37	0.15 0.01	0.1			
C				33.4 1.8	36.8							
N				6.2 0.2	6.25							
Cu	47	300	410	206 33	223 10	125 4	166 14	291 17	151			
Ni	16.3	20	63	232 5	215 21	255 25	220 12	392 16	433			
Cd	1.7	20	98	482 48	311 27	159 7	143 7	316 11	214			
Fe	0.17	2.53	2.73	6.8 0.17	2.93	1.31 0.02	1.23 0.12	7.4 0.7	1.96			
Mn				165 17	146 1	96 7	95 4	209 11	131			
Zn	0.32	6.1	3.75	1.36 0.11	2.26	1.02 0.07	0.64 0.02	1.35 0.02	1.26			
Al	0.39			9	7.7	0.72 0.09	0.94 0.1	12.5 0.3	3.48			
Ba	205				490							

TABLE III-5 Subsamples used for total concentration estimates. \*\*

ANTARCTIC TOWS - (particulates only)

STN M - filter A10 and tubes 3, 19, 26, and 22(for Si).

STN J1- filter A7

STN E - filter A4

GALAPAGOS TOWS

TOW 1 - GA200 + 167

GA201 + 167

T91 + 167 + 158 + 160

T98 + 167

T86 + 154 + 165 + 194

TOW 3 - GA204 + 125

(T119)\* + 125 + 132 + 149 + 135 + 129

(T114) + 125 + 131 + 130 + 118 + 129

MANOP C

TOW 1 - GA217 (for Si)

T49 + X186

T48 + X186 + X198

T47 + X186 + X197

TOW 2 - GA220 (for Si)

T44 + X188 + X175 + X172 + X169 + X176

T43 + X188 + X184 + X189 + X180 + X168

T42 + X185

MANOP S

TOW 3 - GA222 (for Si)

T37 + X110 + X123

T40 + X110 + X127

TOW 6 - GA223,GA224 (for Si)

T30 + X127

\* The  $\text{HNO}_3$ -insoluble residues of T119 and T114 were not analyzed.

\*\* The sum of each subsample series is given in Table III-6, the individual concentrations are tabulated in Appendix II.

Table III-6

Total Concentration Estimates Galapagos Tow 1

	GA200	GA201	T91	T98	T86
Ca	0.89	0.83	0.848	0.81	0.664
P	0.371	0.371	0.428	0.434	0.472
Si	1.28	1.27			
Cu	187 6	197 15	202.8 7.3	267 7.3	176.6 7.6
Ni	229 30	229 20	243 14	231 8.4	226 15
Cd	532 50	(802) 50	499 27	389 32	496 24
Fe	(4.93) 0.1	(5.41) 0.1	7.08 0.41	6.63 0.5	6.71 0.25
Mn	170 30	220 20	153.4 6.1	163.2 5.3	158.4 7.3
Zn	1.3 0.09	1.65 0.16	1.28 0.04	1.35 0.18	1.437 0.067
Al	9 1.8				
Ba					

(continued)

Table III-6

Total Concentration Estimates Galapagos Tow 3

	GA204	T119	T114
Ca	(0.782)	1.36	1.41
P	0.321	0.36	0.36
Si	0.68	[0.0126]*	
Cu	205.5 6.2	229.3 3.9	229.3 5.3
Ni	178 13	231 9.4	226 9
Cd	(631) 34	346 32	293 17
Fe	2.931 0.099	[2.011] 0.058	[1.966] 0.058
Mn	144.7 6.8	145.9 3.8	145.9 3.6
Zn	2.26 0.3	[1.37] 0.12	[1.378] 0.09
Al	7.7 1.2	[0.786] 0.067	
Ba		485 40	

\* Bracketted values were not used in the averages for these elements due to their tendency to resist the nitric acid leaching solution. The residuals of T119 and T114 were not analyzed - only their leaches - (see text).

(continued)

Table III-6

-67-

## Total Concentration Estimates MANOP C Tow 1

	T49	T48	T47
Ca	1.52	1.03	1.48
F	0.28	0.242	(0.397)
Si			
Cu	121.5 8.1	129.8 9.6	125 10
Ni	274 15	272 12	221 13
Cd	153.4 2.6	170.6 4.9	159.6 4.9
Fe	1.312 0.045	1.27 0.1	1.34 0.1
Mn	98 5.5	86 7.1	108 10
Zn	0.946 0.049	(1.597) 0.067	1.086 0.04
Al			0.716 0.086
Ba			

(continued)

Table III-6

Total Concentration Estimates      MANOP C    Tow 2

	T44	T43	T42
Ca	1.51	1.25	1.73
P	0.311	0.289	0.288
Si			
Cu	156.8 5.7	184.6 5.7	155.3 6.8
Ni	233 10	214 11	212 8
Cd	149.2 2.9	134.3 2.7	145.8 3.3
Fe	1.147 0.03	1.391 0.056	(2.048) 0.094
Mn	96.8 4.6	90.3 2.3	98.6 2.8
Zn	0.623 0.016	0.669 0.026	(0.838) 0.033
Al	0.853 0.052	1.049 0.071	(1.59) 0.27
Ba			516 77

(continued)

Table III-6

Total Concentration Estimates      MANOP S    Tow 3

	T37	T40
Ca	3.84	3.47
P	0.427	0.454
Si		
Cu	278 15	311 24
Ni	407 27	376 28
Cd	304 10	326.7 8.7
Fe	8.34 0.69	7 0.27
Mn	196 16	217 10
Zn	1.338 0.056	1.38 0.13
Al	12.9 1.5	12.23 0.74
Ba		

(continued)

Table III-6

Total Concentration Estimates      MANOP S      Tow 6

	T30
Ca	1.58
P	0.363
Si	
Cu	151 13
Ni	433 21
Cd	214.2 4.6
Fe	1.96 0.1
Mn	130.9 4.4
Zn	1.255 0.067
Al	3.48 0.45
Ba	



Significantly higher total trace element concentrations were seen in the plankton samples collected furthest away from the Antarctic Convergence (station locations in Appendix I, Fig. A I-1.). This was in parallel with the increase in water temperature and the decrease in concentrations of dissolved nutrients and trace elements associated with this upwelling regime (Fig. A I-2, A I-3). The analyses of material at site M represent the lowest concentrations of trace elements in bulk surface material ever reported, yet they are collected from an environment which is relatively rich in the dissolved fraction of those elements. The organisms in this tow are very highly silicified, consisting of over 80%  $\text{SiO}_2$  by dry weight. However, some of the labile organic fraction of this plankton was probably released to the suspension seawater, consistent with the low levels of P in the particles.

The total concentrations in two of the Galapagos tows are given in Table III-4. These values are calculated as the sum of all particles and solution fractions and therefore represent true totals. A list of the subsample determinations combined to arrive at these estimates is given in Table III-5 and the total concentration data for each subsample are presented in Table III-6. Specifically, for tow 1, filters GA200 and GA201 as well as centrifuged material in tubes T91, T98, and T86 along with all of their leached fractions were considered in arriving at an averaged total concentration estimate. For tow 3, filter GA204 and tubes T119 and T114 were considered. In general, when arriving at these mean concentrations, if an analysis was greater than 3 standard deviations above the mean of the other subsample values, it

was not used in the final estimate. Few values needed to be rejected by this criterion. Those that were are noted in parentheses in Table III-6. The agreement of the calculated totals to within 10-20% indicates the combined precision of the sample splitting method, sample homogeneity assumption, and the net experimental errors. The residues of the  $\text{HNO}_3$  leach in tubes T119 and T114 from tow 3 were not analyzed, so this series was not used to estimate the totals for elements partially resistant to this solubilization - Si, Fe, Zn, Al. More P is released during the filtration process than during centrifugation, presumably because of greater mechanical lysis during filtration. This can be seen by comparing the total P estimates of centrifuge tubes to filters (both use the centrifuge supernate to estimate the seawater release fraction). Also, analyses of the supernate (188) and the filtrate (183) show higher P in the filtrate.

The total concentrations in the MANOP samples presented in Table III-4 were calculated in the same manner as the Galapagos samples. Only centrifuged material was used for the trace element determinations to eliminate any errors from contamination of filters during handling. The filter subsamples were used for total mass estimation and Si analysis. Specifically, T49, T48, and T47 were used for tow 1; T44, T43, and T42 were used for tow 2; T37 and T40 were used for tow 3; and T30 was used for tow 6. No total concentration estimates were made on material from tows 5 or 7.

This set of plankton analyses from the three Pacific stations represents one of the first comprehensive data sets which include major structural and organic components along with uncontaminated trace

elemental concentrations. In general, the levels of minor components are similar to those reported by Martin and Knauer(1973) and Martin et al.(1976) for plankton tows in the eastern north Pacific Ocean. The levels of Ni, Mn, and Cd in my samples are somewhat higher than those reported by these authors. The differences may be due to the loss of the labile release products to seawater suspensions and washes not analyzed by these authors.

There are significant compositional differences between some of the separate tows at the Galapagos and at the MANOP S site, especially for Al and Fe. This may be related to variability of the surface water masses and atmospheric transport of terrigenous matter to these sites. Changes were noted in the weather and currents while on station at the Galapagos and site S stations. The Galapagos site is subject to excursions of an equatorial surface-water front, discussed by Wyrтки(1967), which affects the organisms and flux of particulate matter out of the surface (Bishop et al, 1980). There was a significant intensification of winds and change in current direction between tows 1 and 3. The MANOP S site is in the transition zone between the Equatorial Countercurrent and the North Equatorial current. There were several days of high winds and rain between the time of tow 3 and tows 6 and 7, possibly indicating effects of the intertropical convergence zone. Surface hydrocasts at the site indicated the presence of a very shallow layer of low oxygen water at the end of the cruise that was not present at the beginning. This water mass was probably of Eastern Pacific origin as opposed to the more oxygenated waters of western origin in the Countercurrent (Tsuchiya,1968).

Changes in the particulate Ca/Si ratio also indicated a variation in the organisms present in the tows.

III-3. LEACHING EXPERIMENTS.

Release of elements to the plankton - sea water suspension.

One of the first results observed in the leaching experiments was the high concentration of many of the elements in the sea water in which the plankton were suspended. These elements were initially associated with the particles when the plankton were collected and were released to the sea water suspension during the two hours it took to get the samples into the ship's laboratory for processing. These results are summarized in Table III-7a,b,c and Figs. III-1 to III-6. The data are expressed as the percentage of the estimated total particulate element which was released to the sea water separated from the plankton sample. Also noted is the time from the end of the tow, in hours, to the time of separation. All of the samples shown in the figures were stored in the dark at 4 degrees (C) from the time they were collected until they were filtered or centrifuged.

The first observation of this release was in the Galapagos samples where significant amounts of the total P, Cd, Ni, and Mn were found in the sea water only six to eight hours after completion of the tow. A sample stored for 24 hours (Tow 1, T86) lost over 70% of its P, 50% of its Cd and Mn, and more than 30% of its Ni. In anticipation of these releases, several experimental changes were made at the MANOP stations: more rapid sample processing, documentation of times during processing, and several experiments following the history of regeneration of elements in solution over significantly longer time periods. The results for one of the timed experiments (MANOP S, Tow 6) are noted in

Table III-7a,b,c. Seawater Release Percentages

Percentages of the total element released to the seawater suspension.

(Multiple columns for one seawater solution are based on the different estimates of the total concentration of each tow; values listed below each percentage are the 95% confidence limits)

Tows	Seawater sample number	Total concentration estimate
Galapagos Tow 1	167	T91
	167	T98
	154	T86
Tow 3	125	GA204
	125	T119 (1)
	125	T114 (1)
MANOP C Tow 1	186	T49
	186	T48
	186	T47
Tow 2	188	T44
	188	T43
	185	T42
MANOP S Tow 3	110	T37
	110	T40
Tow 6	127	T30
	136	T30
	125	T30
	140	T30
	76	T30

(1) The particulate residues of T119 and T114 were not analyzed, so these totals were not used for estimates of Si, Fe, Zn, or Al release.

(Table III-7a,b,c. continued on next pages)

Table III-7a

Seawater Release Percentages Galapagos Tows 1,3

	167	167	154	125	125	125	125
Ca	0	0	7.26		1.17		1.13
P	36.8	39.9	76.9	50.2	44.8		44.8
Si				0.474			
Cu	18 2.8	15.1 2.3	18.9 3	15.1 1.2	13.59 0.99	13.59 0.99	13.59 0.99
Ni	11.7 1.4	13.5 1.6	35.1 5.4	27.4 3.7	21.1 2.4	21.1 2.4	21.6 2.5
Cd	26.3 3.2	37.2 5.1	55 4.5		17.6 2	17.6 2	20.8 1.9
Fe	0.372 0.075	0.438 0.091	0.936 0.087	4.57 0.27			
Mn	12.6 2.2	13 2.2	53.6 5	38.1 2.2	37.7 1.5	37.7 1.5	37.7 1.4
Zn	8 0.88	8.2 1.3	12.8 2	5.75 0.9			
Al				0.192 0.038			
Ba					3.44 0.81		
time (hours)	8	8	24	4	4	4	4

Table III-7b  
Sewater Release Percentages MANOP Tows 1-3

	X186	X186	X186	X188	X188	X185	X110	X110
Ca	0	0	0	0	0	0	0	0
P	24.9	30.3		13.2	12.2	14.4	14.9	14.9
Si								
Cu	14.8 3.6	14.6 3.6	17 4.3	10.4 1	7.68 0.8	9 1.1	9.1 2	8.6 2
Ni	12.9 1.6	13.7 1.7	18.9 2.5	17.1 2.5	15.9 2.4	12.2 1.6	8.5 1.5	9.7 1.8
Cd	24.27 0.75	22.95 0.88	27.4 1	6.88 0.17	6.55 0.16	4.4 0.2	9 1	8.99 0.99
Fe	5.85 0.94	6.3 1	6.6 1	4.38 0.13	3.09 0.12		1.4 0.3	2.08 0.43
Mn	13.4 3.4	16.1 4.3	14.3 3.8	9.08 0.78	8.33 0.64	7.08 0.64	14.5 2.6	13.9 2.3
Zn								
Al				6.4 4.2	4.4 2.9			
Ba								
time	4	4	4	2	2	2	2	2



Table III-7c

Seawater Release Percentages		MANOP Tow 6			
	X127	X136	X125	X140	X76
Ca	0	0	0	0	0
P	34.3	50.9	70.4	80.6	78.3
Si					
Cu	20.8 2.1	11.6 2.7	9.4 1.9	20.8 2.4	9.9 1.6
Ni	23.5 4.2	34.4 3.4	38.7 3.4	46.6 4.6	49.3 4.5
Cd	9.43 0.52	16.1 1	24.42 0.75	23.9 1.2	22.39 0.84
Fe	4.56 0.44	7.14 0.59	9.72 0.74	11.99 0.78	8.72 0.85
Mn	20.1 1.8	37 3.8	48.2 1.7	54.6 2.1	49.8 4.2
Zn					
Al					
Ba					
time	2.5	12	24	72	96

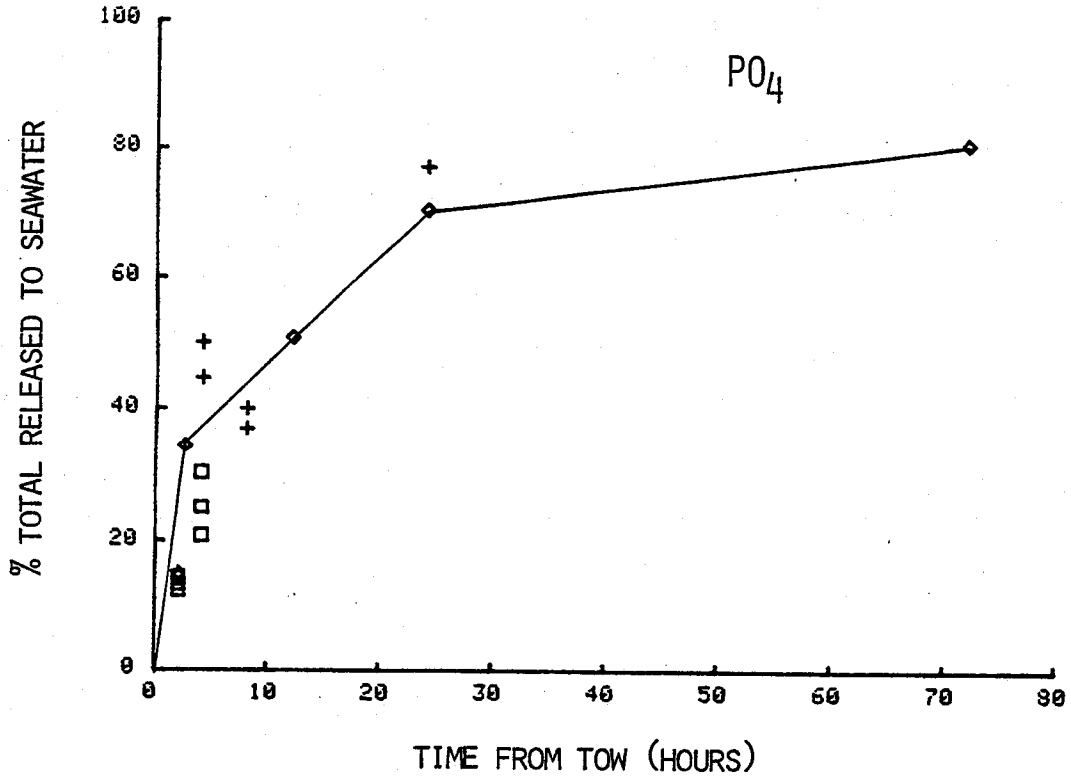
Figure III-1. Seawater release:  $PO_4$  and Cd vs. time.

SYMBOL KEY  
(for figures 1 - 6)

- + Galapagos Tow 1 & 3
- MANOP C Tow 1 & 2
- △ MANOP S Tow 3
- ◇ MANOP S Tow 6 (points connected)

Lines superimposed on points represent 95% confidence limits in the percentage.

A



B

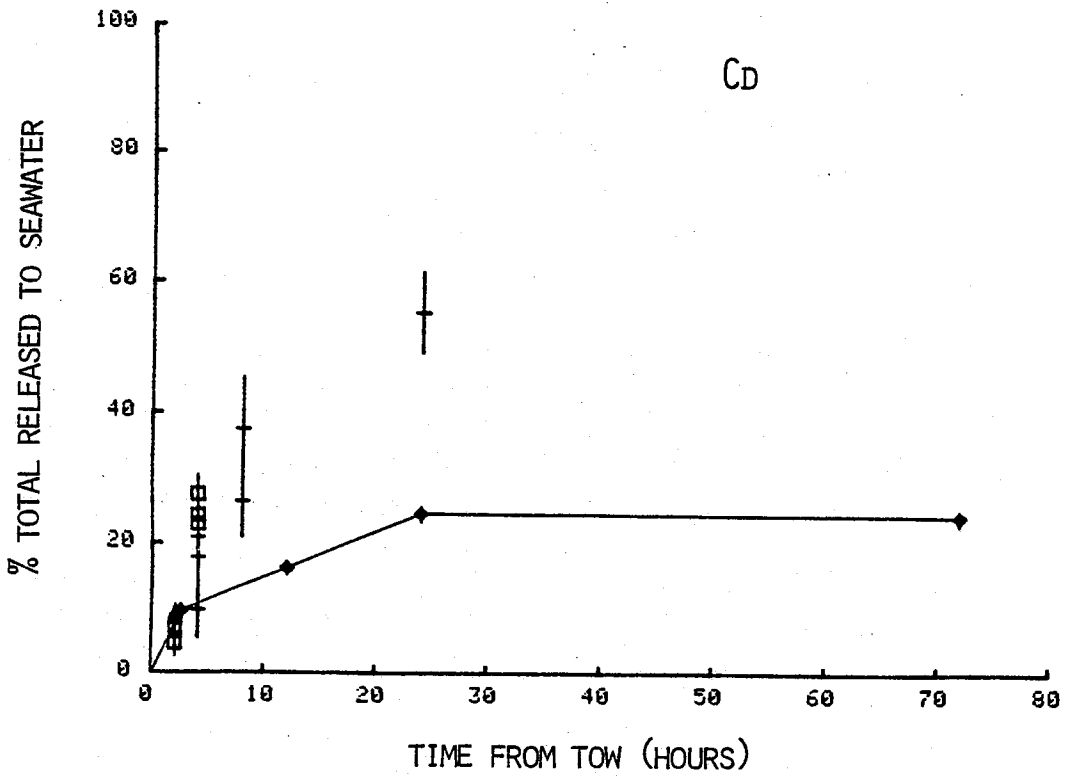


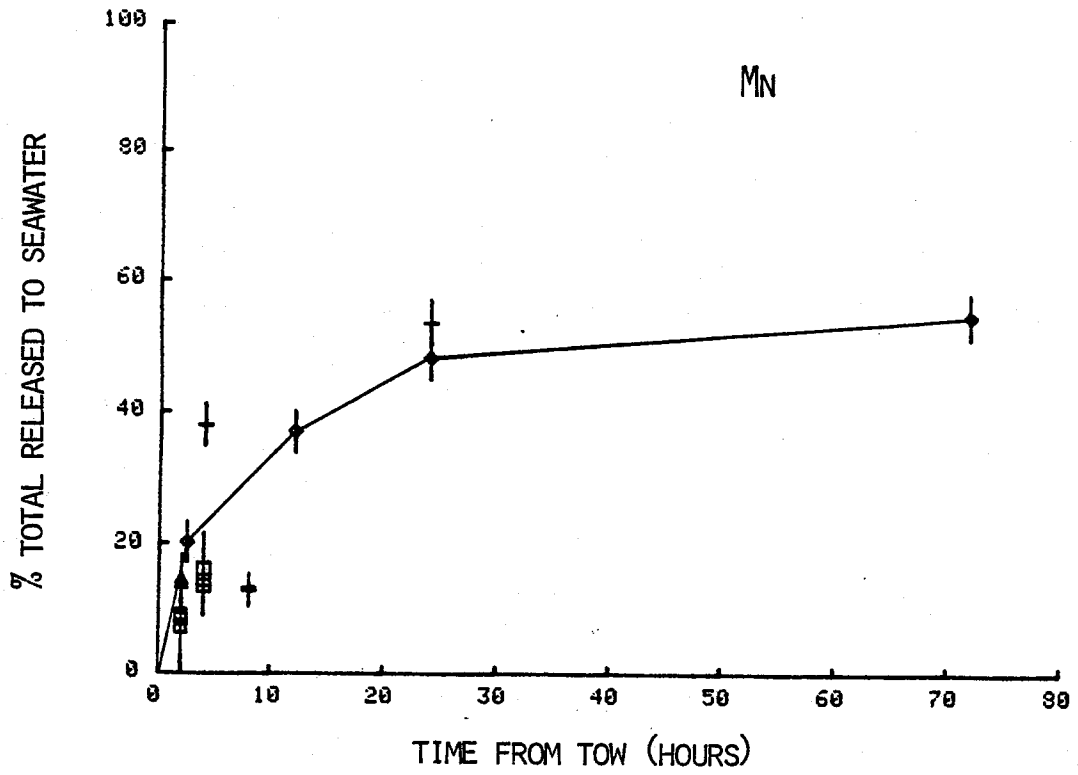
Figure III-2. Seawater release: Mn and Ni vs. time.

SYMBOL KEY  
(for figures 1 - 6)

- + Galapagos Tow 1 & 3
- MANOP C Tow 1 & 2
- △ MANOP S Tow 3
- ◇ MANOP S Tow 6 (points connected)

Lines superimposed on points represent 95% confidence limits in the percentage.

A



B

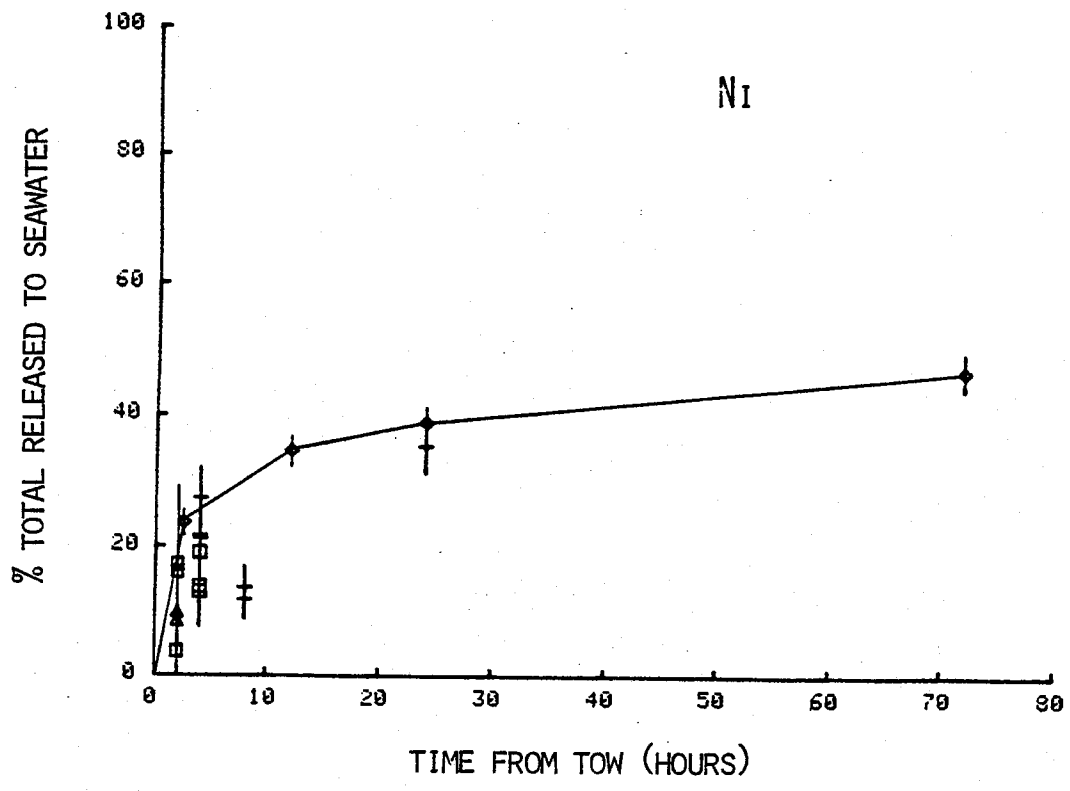


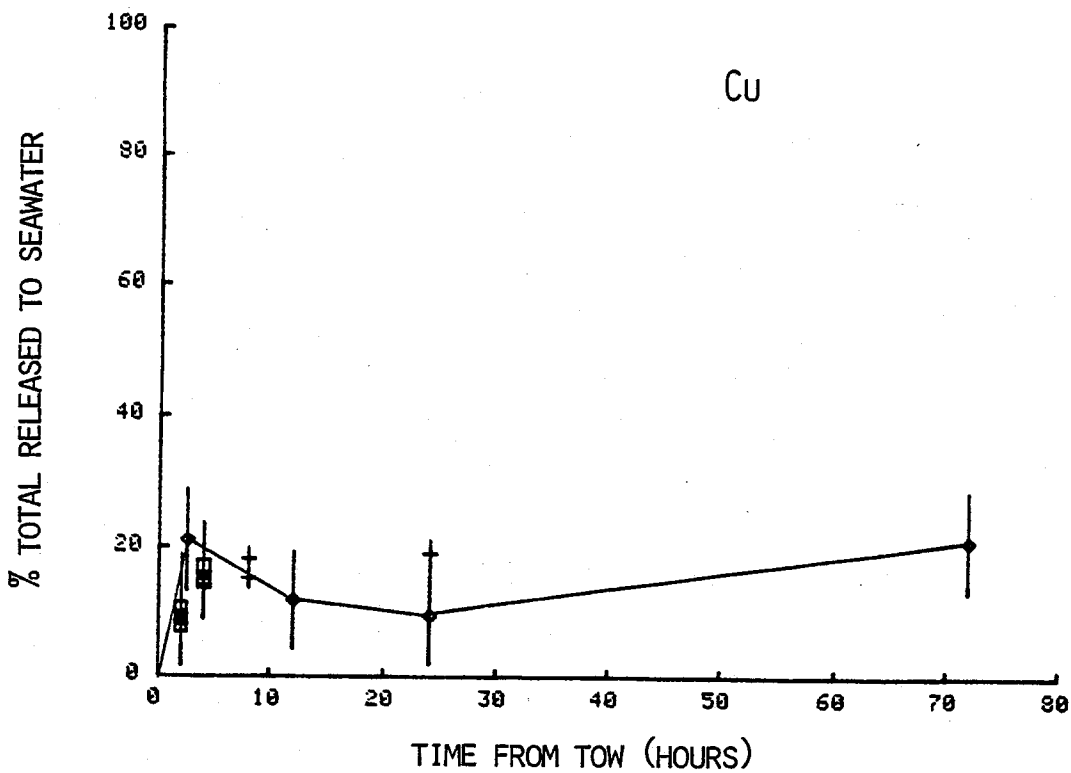
Figure III-3. Seawater release: Cu and Fe vs. time.

SYMBOL KEY  
(for figures 1 - 6)

- + Galapagos Tow 1 & 3
- MANOP C Tow 1 & 2
- △ MANOP S Tow 3
- ◇ MANOP S Tow 6 (points connected)

Lines superimposed on points represent 95% confidence limits in the percentage.

A



B

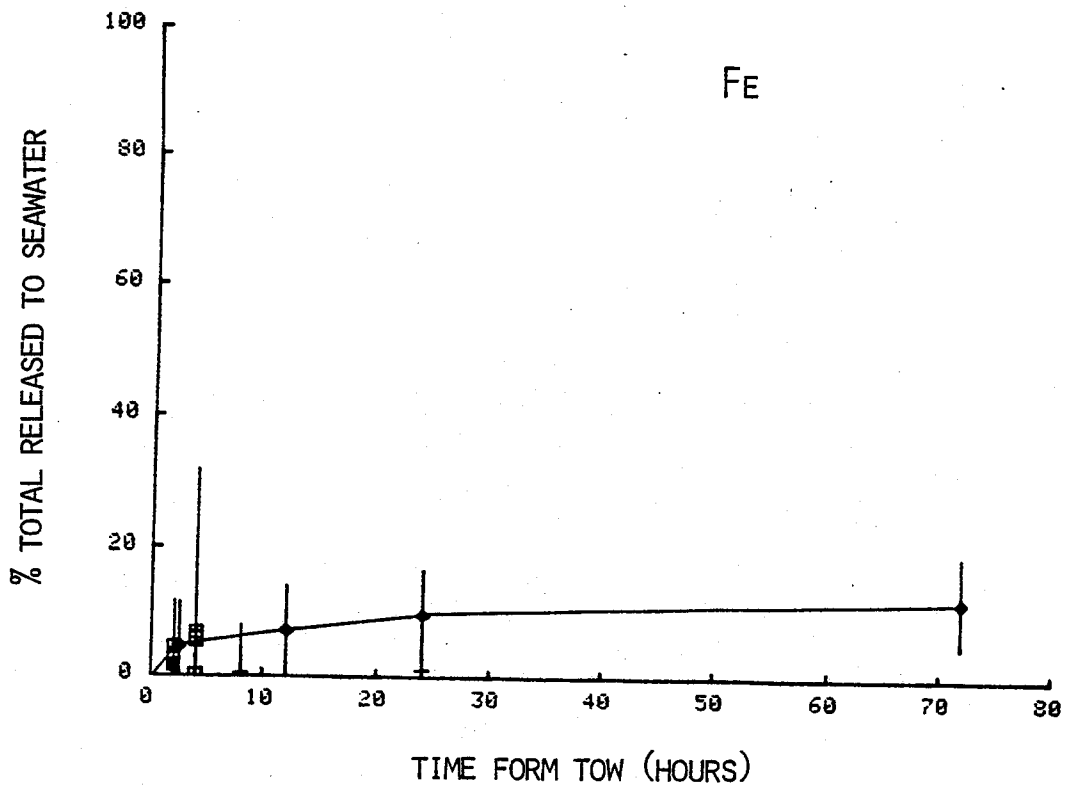


Figure III-4. Seawater release: Zn and Al vs. time.

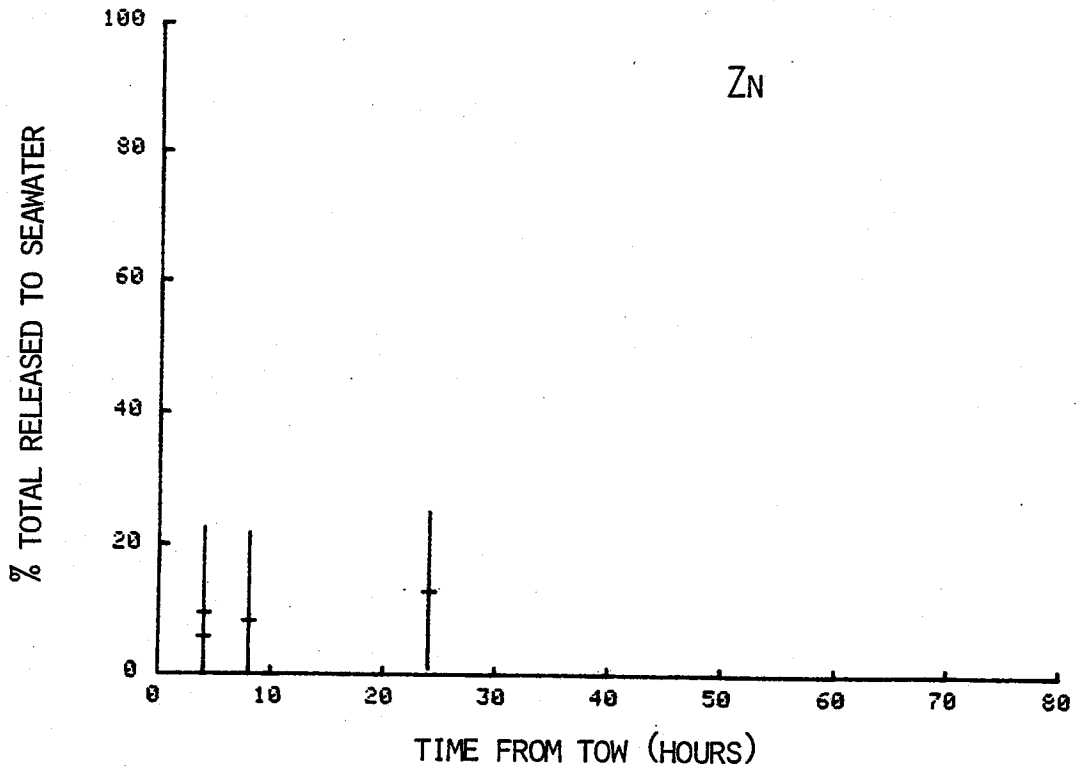
SYMBOL KEY  
(for figures 1 - 6)

- + Galapagos Tow 1 & 3
- MANOP C Tow 1 & 2

Lines superimposed on points represent 95% confidence limits in the percentage.



A



B

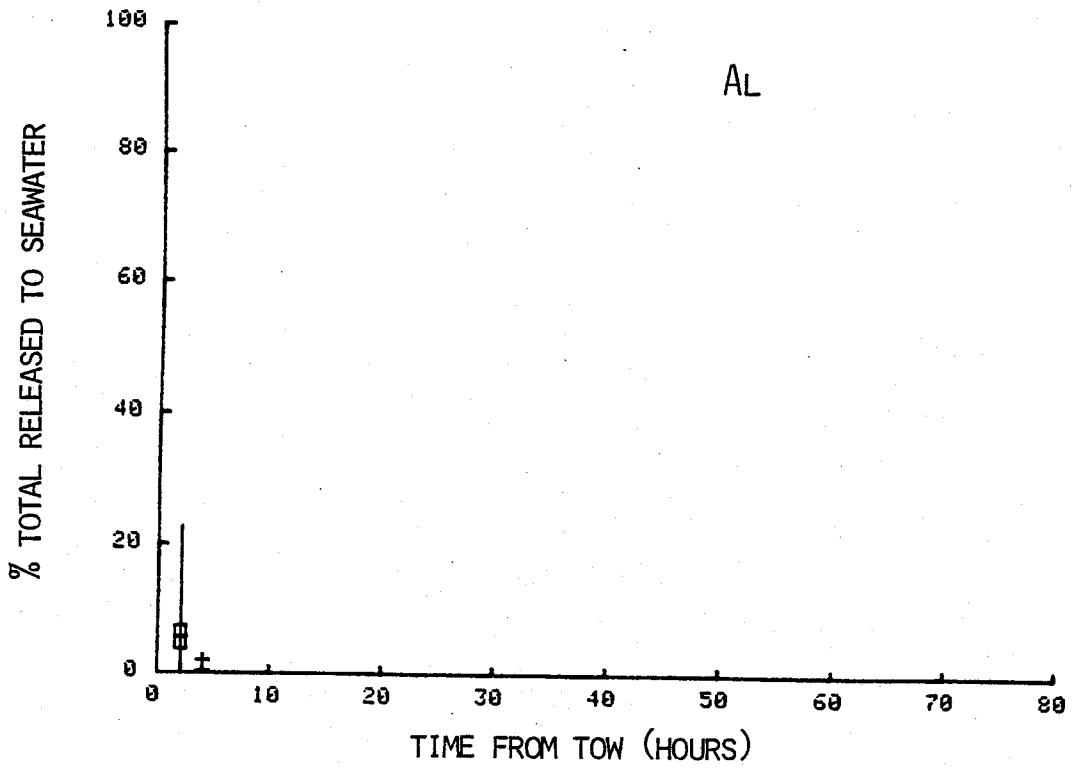


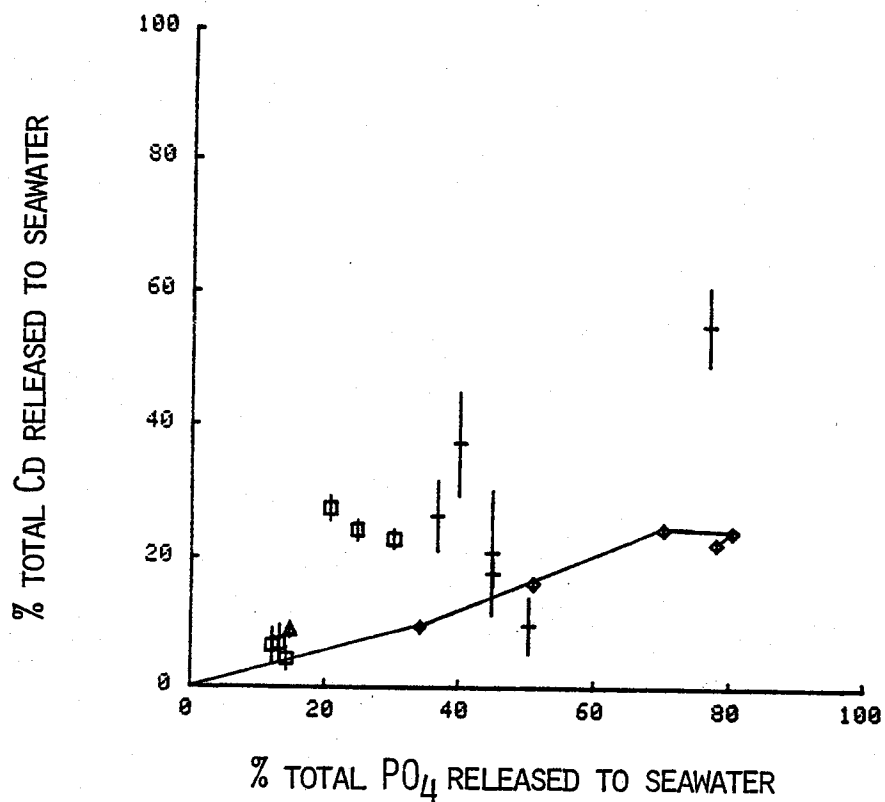
Figure III-5. Seawater release: Cd and Mn vs. P.

SYMBOL KEY  
(for figures 1 - 6)

- + Galapagos Tow 1 & 3
- MANOP C Tow 1 & 2
- △ MANOP S Tow 3
- ◇ MANOP S Tow 6 (points connected)

Lines superimposed on points represent 95% confidence limits in the percentage.

A



B

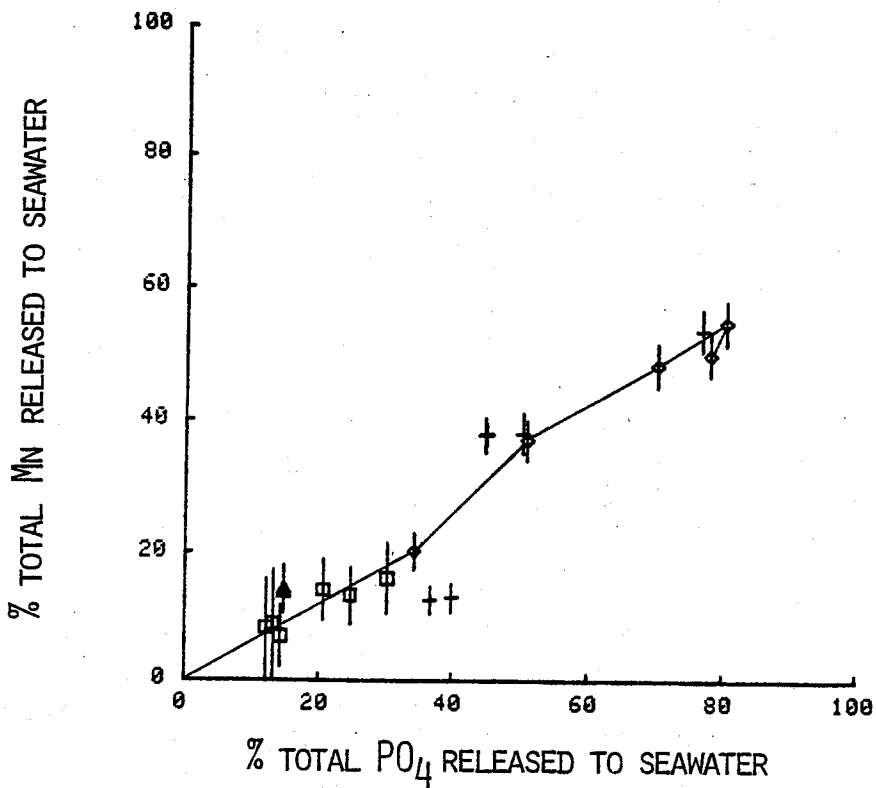


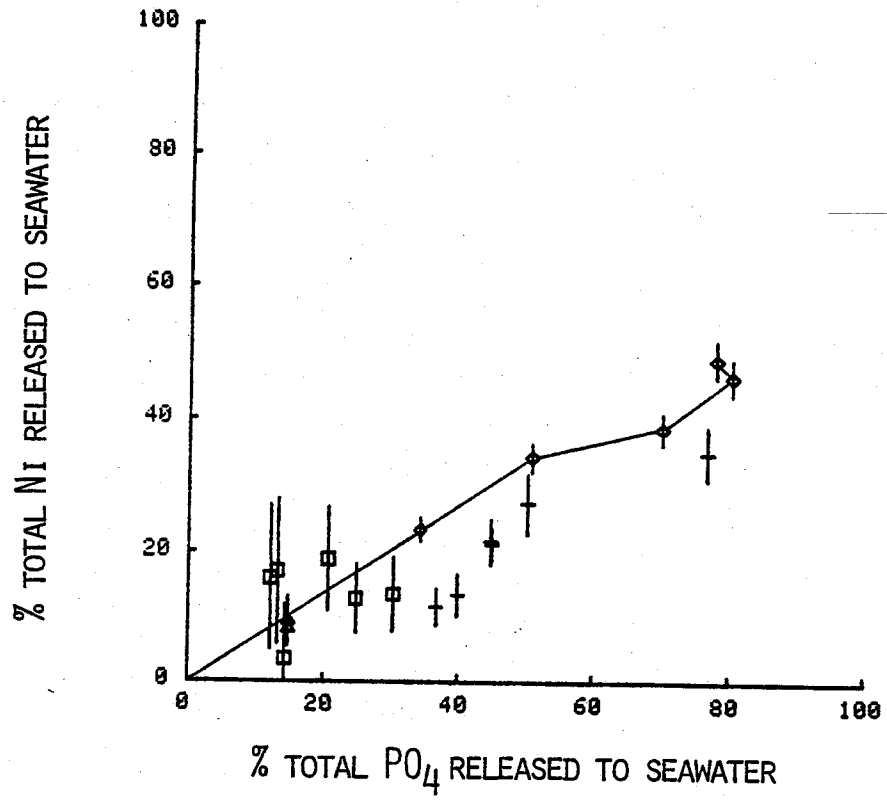
Figure III-6. Seawater release:  $PO_4$  and Mn vs. Ni.

SYMBOL KEY  
(for figures 1 - 6)

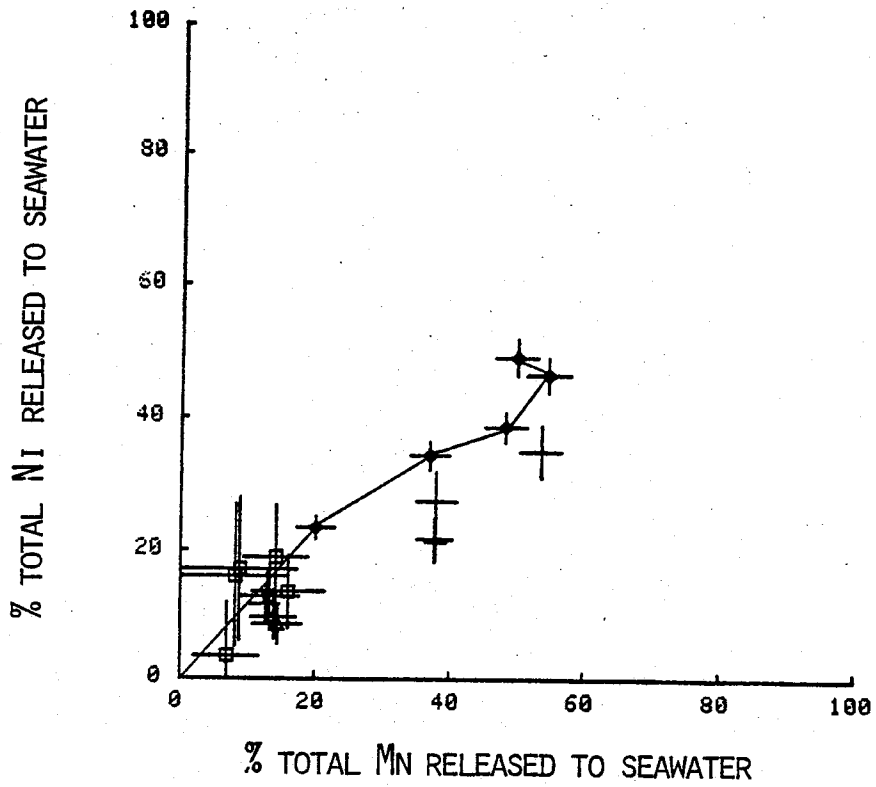
- + Galapagos Tow 1 & 3
- MANOP C Tow 1 & 2
- △ MANOP S Tow 3
- ◇ MANOP S Tow 6 (points connected)

Lines superimposed on points represent 95% confidence limits in the percentage.

A



B



the figures by the five points connected by lines. The material in this experiment was handled identically to the normally processed centrifuged samples. It was subsampled to a set of five centrifuge tubes, two hours after the tow and was kept cold and in the dark until the time of centrifugation. The last sample, centrifuged at 96 hours, was not properly acidified for storage after collection, and precipitates formed. The sample was spiked in the lab with strong acid to solubilize any precipitated metals but the effectiveness of this is not known. The concentrations of most of the elements in this sample decreased slightly from the levels in the 72-hour sample. This could be due to the precipitation or to a cessation of the release.

As in the Galapagos experiments, P, Mn, Ni, and Cd were rapidly transferred from the particles to the sea water in the MANOP samples (Figs. III-1, III-2). The quantity of each element released approached a constant value within several tens of hours. Data from all experiments carried out under these conditions are plotted as individual points along with the MANOP time-series experiment in the figures. The behavior of each element was similar from experiment to experiment, except in Tow 6, where the relative release of Cd was lower than in other experiments.

In contrast to the behavior of these labile elements, significantly less of the Cu, Fe, Zn, Al, and Ba were solubilized in the sea water (Figs. III-3, III-4). There was always an initial pulse of Cu released along with the labile elements, but its concentration would then decrease with time by some secondary process. The amount of Fe in the sea water was always very small with respect to its total

particulate concentration. The small fraction which was released maintained a constant ratio to P and the other labile elements. The concentrations of Zn, Al, and Ba detected in the sea water were low and non-systematic, being near their limits of detection.

Figs. III-5 and III-6 show the relative increase of the elements plotted against the P released, and Table III-8 gives the atomic ratios of each of these labile elements to the P in the sea water solution. The ratios were essentially constant throughout the MANOP Tow-6 time series experiment (samples 127-76). This would imply that these elements are being released from sites which are behaving as a single pool of labile material. Although there is some variability in the ratios between tows, the Cd/P and Ni/P ratios generally are similar to those of the dissolved species in the upper ocean. The initial release of Cu followed by its retention on the particles can be seen as a constantly decreasing ratio to P with time. Although the regeneration of Fe relative to its total particulate concentration is small, the fraction released has a relatively constant ratio to P.

Several more experiments were carried out to characterize the nature of the release. An attempt was made in MANOP S, Tow 7 to assess the effect of bacterial activity, temperature, and light on the release experiments. An antibiotic mixture of chloramphenicol, penicillin, and streptomycin was injected into a set of subsamples which were treated in a manner similar to the Tow-6 time series. Although these samples were contaminated for Cd, the release of Mn and Fe were similar to that observed in Tow 6. However, the total solubilized P over the same time period was only 17%, of which 14% had been released by the time the

Table III-8. Elemental ratios in seawater suspensions. (x10<sup>-3</sup>)

Atom ratios x10<sup>-3</sup>, ( ) are 95% confidence limits in the ratio.

		Cd/P ratio	Mn/P ratio	Ni/P ratio
Galapagos	167	0.84 (.10)	0.12 (.02)	0.18 (.02)
	154	0.75 (.06)	0.23 (.02)	0.22 (.03)
	125	0.38 (.03)	0.34 (.02)	0.30 (.04)
MANOP C	186	0.53 (.02)	0.19 (.05)	0.51 (.06)
	188	0.25 (.01)	0.21 (.02)	0.96 (.15)
	185	0.15 (.01)	0.17 (.02)	0.62 (.09)
MANOP S	110	0.43 (.05)	0.45 (.07)	0.54 (.10)
	127	0.16 (.01)	0.21 (.02)	0.82 (.15)
	136	0.19 (.01)	0.26 (.03)	0.81 (.08)
	125	0.20 (.01)	0.25 (.01)	0.66 (.05)
	140	0.18 (.01)	0.24 (.01)	0.69 (.07)
	76	0.17 (.01)	0.23 (.02)	0.75 (.06)
water column		0.32-0.37(i)	0.5-1.5(ii)	1.0 (iii)

		Fe/P ratio	Cu/P ratio
Galapagos	167	0.17 (.03)	0.23 (.04)
	154	0.17 (.01)	0.09 (.02)
	125	0.83 (.05)	0.19 (.02)
MANOP C	186	1.1 (.2)	0.26 (.06)
	188	1.2 (.04)	0.40 (.04)
	185	0.77 (.13)	0.34 (.04)
MANOP S	110	1.8 (.4)	0.40 (.09)
	127	0.72 (.06)	0.25 (.02)
	136	0.76 (.05)	0.10 (.02)
	125	0.74 (.05)	0.06 (.01)
	140	0.80 (.04)	0.11 (.01)
	76	0.60 (.05)	0.05 (.01)
water column		?	0.5-0.8(iv)

(i) Pacific, water column (Boyle et al,1976; Bruland et al,1978)

(ii) Pacific, oxygen minimum (Klinkhammer and Bender,1980)

(iii) Pacific, upper water column (Sclater et al,1976)

(iv) Pacific, upper water column (Boyle et al.,1977)



samples were spiked with antibiotics. Although insufficient controls were performed on this experiment, it suggests that some component of the release process is a result of bacterial oxidation of the organic matrix.

The implications of this remineralization process must be considered during the sampling and handling of organic particulate matter for trace analysis by towing, filtration, and trapping. The rapid release of these elements requires careful containment of the sample and complete mass balancing from the time of collection if their chemistry in the upper oceans is to be studied. Variations in sampling techniques will surely result in large variations in the collected concentrations of P, Ni, Cd, Mn, and perhaps other trace species. Washing the sample removes these released elements and, as will be discussed, causes even more extensive release. This rapid solubilization, along with sample contamination, probably accounts for much of the variability seen during the long history of reported plankton elemental analyses.

#### Filtration of the sea water-plankton suspension.

To further characterize the form of the elements released to the sea water, three sets of filtration experiments were performed. First, a comparison was made between the two methods of concentrating the plankton from suspension: direct filtration and suspension. Second, the centrifuged sea water suspension solution was passed through a series of progressively smaller membrane filters. Third, a subsample of a sea water suspension solution was passed through an

ultrafiltration membrane (Millipore, CX immersible, Pellicon type PTGC, nmwl 10000). The results of these experiments are summarized in Table III-9, expressed as the percentage of an element in the sea water suspension which passed through each filter.

As already mentioned in the discussion of total elemental concentrations, the process of filtration releases more P than does centrifugation. This effect can be seen here by comparing the filtrate (X183) with the supernate (X188) which is used as the reference starting material for the percentage calculations in column 1 of Table III-9. A much larger amount of P is released to the filtrate, as are larger amounts of the labile trace elements, although their enrichment is less extreme. The difference seen between the two collection methods is probably due to mechanical lysis of the cells under vacuum filtration releasing dissolved and very small particulate cellular material, which then passes through the filter. This is consistent with a model whereby lysis and release of cell fluids is a major process determining the observed regeneration of elements.

Filtration of the centrifuged sea water suspension gave rough estimates of the size distribution of the released elements. Except for Cd, greater than 90% of the rapidly released elements passed through the 1.0 $\mu$ m filter. This demonstrated that the metals were not associated with large, non-centrifugable organic particles which were carried over in the aspiration procedure. As the filter pore size decreased, each element was more efficiently removed. The maximum removals ranged from only 20% for P, to 85% for Cd. No specific estimates of the size of the materials removed from the sea water can

Table III-9. Filtration Experiments

Percentage of each element in the seawater suspension which passes through each filter. (X188 is the reference starting material to which these are normalized). (i)

X183 direct filtr. of plankton (0.4 $\mu$ m)		X171 (1.0 $\mu$ m)	X182 (0.1 $\mu$ m)	X163 (0.05 $\mu$ m)	X177 ultrafilt.
152%	P	93%	83%	80%	77%
112 (14)	Mn	96 (13)	82 (11)	69 (30)	75 (19)
135 (17)	Ni	102 (13)	71 (15)	68 (14)	{106}
116 (25)	Cu	93 (20)	39 (20)	{100}	36 (10)
112 (9)	Cd	68 (6)	12 (5)	15 (2)	25 (5)
	Fe				45 (10)

(i) Values listed in parenthesis ( ) are the 95% confidence limits of the percentage. Values listed in braces { } are suspected of contamination.

be made, since these filters are not well characterized with respect to adsorption of metals and organic matter from solutions. Sizing is also uncertain because of clogging of the membranes as filtration proceeds. This was noticeable after only 1-2 ml of solution had been filtered. However, significant amounts of the released elements clearly pass through these membranes and meet the frequently-used operational definition of dissolved species.

Releases during resuspension of planktonic material.

Several experiments were performed which involved the resuspension of the centrifuged plankton in solutions which included: more surface sea water; sea water with millimolar EDTA; isotonic ammonium chloride; and distilled water. The results of these experiments are given in Tables III-10 and III-11.

Subsamples from MANOP S, Tow 3 were resuspended two hours after the tow in surface sea water collected from that site. The suspensions were left in the centrifuge tubes at room temperature for two hours before collection of the "fresh" suspension sea water by centrifugation. One of the subsamples contained only surface sea water and another contained a solution of  $10^{-3}$  M EDTA made up in the same surface sea water. The releases to the resuspension sea water can be seen as a continuation of the time dependent process discussed in the last section. Most of the elements show a solubilization (Table III-10) which is equivalent to that in the single-step sea water release experiments, but Cd shows a significantly higher concentration with an associated increase in the Cd/P ratio.

Table III-10. Resuspension in Seawater-EDTA solutions

Percentage of total particulate element released to solution.

	Original seawater		Resuspension seawater		Resuspension seawater w/EDTA	
	X110	metal/P ( $\times 10^{-3}$ )	X117	metal/P ( $\times 10^{-3}$ )	X123	metal/P ( $\times 10^{-3}$ )
Ca	0		0		0	
P	14.9		25.9		26.9	
Cu	8.9	.40	14.4	.38	15.9	.39
Ni	9.1	.54	12.7	.41	21.4	.75
Cd	9	.43	29.6	.82	47	1.2
Fe	1.7	1.8	2.1	1.0	3.1	2.2
Mn	14.2	.45	13.8	.26	33.1	.56

Table III-11. Distilled Water Release Percentages.

	Galapagos Tow 3			MANOP C Tow 1		Tow 2		
	125 (sw)*	131 (dw)	132 (dw)	X186 (sw)	X197 (dw)	X188 (sw)	X184 (dw)	X175 (dw)
Ca	1.2	3.8	4.6	0	1.2	0	0	6.7
P	47	27	29	28	36	13	33	69
Cu	14	8.9	9.7	15	16	17	38	57
Ni	23	12	13	15	32	17	38	57
Cd	19	10	10	25	17	6.7	26	34
Fe	4.6	4.0	4.3	6.3	7.1	3.7	6.8	10
Mn	38	21	22	15	30	8.7	30	54
Zn	5.8	3.3	4.1				21	22
Si	.47	.38	.41					
Al	.19	.14	.22			5.4	2.0	2.2
Ba	3.4		4.9					
	time 4hrs.	1hr.		4hr.	1/2hr.	2hr.	1/2hr.	8hr.

\* "(sw)" indicates a seawater suspension supernate.  
 "(dw)" indicates a distilled water supernate.

Addition of the strong metal chelator, EDTA, to the system has no effect on the process which is causing the P release. This is reasonable, since there is no binding of phosphate species to the EDTA ligand. Cu and Fe do not show any significant differences in their release to the sea water with or without EDTA present, even though, among the metals studied, these form the strongest chelates with EDTA. The more labile elements Ni, Cd, and Mn all show significant increases in concentration in the EDTA compared to the sea water solution alone. The deterioration of structural organic membranes exposed to EDTA solutions has been noted (Hughes, 1972). This was attributed to the extraction of divalent cations from sites which cross-link adjacent carboxylate functions in these membranes. The increased removal of metals from the plankton to the EDTA solution could be an example of this or of removal from another adsorbing site on the surface.

In an experiment with cultured phytoplankton, Davies(1970) showed that a millimolar EDTA solution solubilized precipitated Fe from the surfaces of the plankton within several tens of minutes after its addition to the cultures. This was not seen in the leaching experiments, and clearly very little of the Fe in the MANOP samples is in a freshly precipitated, chelatable form. Since the metal/Fe ratio in all of the release products discussed so far is always low ( $\leq 5$ ), it is unlikely that any of the other trace metals are homogeneously coprecipitated in an Fe-hydroxide matrix which is being solubilized by the leaching solutions. The increased removal of Ni, Cd, and Mn must be due to their association with surface sites which are less stable or physically more exposed than those sites binding the Cu and the Fe to

the particles.

Releases to distilled water.

Several of the subsamples were resuspended in a distilled water wash after separation from the plankton-sea water suspension. The results of these experiments are summarized in Tables III-11 and III-12. The elements P, Ni, Cd, and Mn, which were rapidly solubilized in the sea water suspension, were also extracted into the distilled water. The concentration of the labile elements in the distilled water was inversely related to the percentage of these elements which had already been released to the sea water. In general, the metal/P ratio was the same in both the sea water and distilled water. This behavior is consistent with a model of release or exposure of material by lysis of cell membranes. This is occurring even while the sample remains in the sea water suspension due to mechanical, bacterial, or autolytic decomposition, but is accelerated by suspension in the distilled water. The results of this experiment are significant considering the frequently used experimental practice of washing plankton samples with distilled water to reduce analytical interferences from sea salt. It can be expected that a significant but variable amount of these labile elements will be lost to any distilled water wash.

The cumulative transfer of elements to the sea water and distilled water solutions from the plankton was of the same order as the maximum release seen in the long-term sea water suspension experiment. Calculation of the ratios of cumulative Cd/P solubilized by the combined solutions (Table III-12) yields ratios which are close to



Table III-12. Distilled Water Release - Metal/P Ratios (x10<sup>-3</sup>)

	Galapagos Tow 3			MANOP C Tow 1		Tow 2		X175 (dw)	water column*
	125 (sw)	131 (dw)	132 (dw)	X186 (sw)	X197 (dw)	X188 (sw)	X184 (dw)		
Cu	.19	.21	.21	.26	.14	.40	.39	.18	.7
Ni	.30	.26	.28	.51	.50	.96	.85	.62	1.0
Cd	.38 (cumulative sw + dw)	.38 (.38)	.36 (.38)	.53	.19 (.32)	.25	.37 (.33)	.23 (.24)	.35
Fe	.83	1.3	1.3	1.1	.68	1.2	1.0	.56	
Mn	.34	.33	.32	.19	.23	.21	.29	.24	1.0
Zn	.81	.8	.94				1.5	.64	2
Ba			.24						

\*

Approximate upper-ocean water column ratios  
from references given in Table III-8

those observed in the water column, although there is more variability in the individual solution ratios.

In the typical leaching experiment, the total time of exposure to each leaching solution was forty-five minutes (3 resuspension steps, 15 minutes each). Using two subsamples of MANOP C, tow 2, an 8 hour total exposure time was compared with the shorter period for each leaching solution. Significantly more of the labile components were found in the distilled water solution which was in contact with the sample for 8 hours. This is consistent with the observed time-dependence of the sea water releases. The net release of these elements ranged from 40% to 80% for Cd, Mn, Ni, and P. Again, the relative amount of Cu in these solutions was lower than that of the labile elements, and the drop in the Cu/P ratio in the long exposure solution showed the tendency of Cu to stay in the particulate phases.

The behavior of the labile elements was further studied in an experiment comparing isotonic  $\text{NH}_4\text{Cl}$  with distilled water resuspension (Table III-13). If a significant amount of the rapid releases seen were due to lysis alone, then the suspension of the plankton in an iso-osmotic solution should reduce the release relative to that in distilled water. Clearly, any reduction in release due to the maintenance of osmotic equilibrium in this wash should not go below the continued rate of regeneration seen in the sea water resuspension experiment. Comparison of the P in the distilled water and  $\text{NH}_4\text{Cl}$  solutions shows the dramatic effect that lysis has - nearly doubling the release of this element to distilled water. In contrast to the behavior of P, noticeably more Cu, Ni, Cd, and Mn were released to the

Table III-13. Isotonic Ammonium Chloride Leaches.

Percentage released to solution and metal/P ratios. (MANOP C Tow1)

	Seawater		Distilled water		NH <sub>4</sub> Cl	
	X186	metal/P	X197	metal/P	X198	metal/P
Ca	0		1.2		1.6	
P	27.5		35.9		19.2	
Cu	15.5	.26	16.1	.14	26.9	.75
Ni	15.2	.51	32.2	.50	40	2.3
Cd	24.9	.53	17.1	.19	28	1.0
Fe	6.3	1.1	7.1	.68	6.3	1.7
Mn	14.6	.19	29.8	.23	34.2	.63

NH<sub>4</sub>Cl solution. This apparent exchange of cations from surface sites suggests a relatively labile surface complex for Ni, Mn, and Cd but is inconsistent with the otherwise resistant behavior of Cu in the sea water suspensions, EDTA, and distilled water. Again, there was no detectable effect on the release of Fe.

A final experiment performed on the MANOP S material involved the resuspension of subsamples in surface sea water with and without the addition of another strong metal chelator - ammonium pyrrolidinedithiocarbamate (APDC). A volume of chloroform was then added to each suspension to extract any non-polar metal organic complexes from the system. The small volumes involved and the difficulty of the direct A.A. analysis in the organic matrix made quantifying the results of this experiment difficult, but several features of the results are still important (Table III-14). The release to the sea water-chloroform system without APDC was similar to that seen in the other sea water resuspension experiments. Also, no metals were directly extracted from this sea water suspension into the organic solvent. This indicates that the majority of the metals released to the sea water are not associated with extractable non-polar organic molecules. The extracted sea water which contained the APDC had lower concentrations of the released metals as did the residual particulates. These metals were easily detected in the chloroform extract. It is clear that significant amounts of the Ni, Mn, and Cd bound to the particles and released to the sea water suspension can be chelated by APDC and only then are extractable into organic solvents. The Fe released to the sea water was not extracted directly into the

Table III-14. Seawater Suspension - APDC - Chloroform Extraction

Total element in each fraction (nanomoles)

	Seawater suspension	Resuspension seawater	CHCl <sub>3</sub> extract (i)	Particulate residue
	X129	X121 / X128	XT34 / XT35	T35 / T35
Cu w/o APDC	0.79	0.51	0 (<0.1)	10.3
w/ APDC			2.4	5.5
Ni w/o APDC	5.5	7.3	0	22.1
w/ APDC		0.57	2.1	22.4
Cd w/o APDC	9.0	12	0	5.1
w/ APDC		1.7	.12	3.7
Fe w/o APDC	10	3	0	171
w/ APDC		4	(<.5)	186
Mn w/o APDC	1.9	5	0	10.7
w APDC		.17	.45	5.2

(i) The analysis in the organic solvent was only semi-quantitative.

chloroform, nor was it chelated by the APDC.

A subsample of the plankton from Galapagos, Tow 1, was extracted with ethanol, removing photosynthetic pigments and low molecular weight organic acids and sugars (Wallen and Geen, 1971). No more than 1% of any of the trace elements was extracted by this solution and less than 5% of the P. This sample had already been stored for 24 hours and washed with distilled water, so much of the more labile material had already been released. Another subsample of material from MANOP C, Tow 2, was separated from the seawater suspension and immediately extracted with ethanol. The mixture was heated to 60 degrees (C) and ultrasonified at intervals over a two hour period. The ethanol extract, which was bright green at this point, was analyzed for Cd and none was detectable beyond the small amount carried over from the seawater suspension. Clearly, very little of the metals investigated are strongly bound to any extractable organic molecules.

#### Acid leaching series.

Sample splits from Galapagos, Tow 3, and MANOP C, Tow 2, were processed through a series of distilled-water leaches followed by acid solutions of increasing strengths. Specifically, the complete sample mass balance includes: the seawater supernate; distilled water;  $10^{-3}$  N HCl; 0.1N HCl; 16N HNO<sub>3</sub>; and the insoluble residue. The processing was done at room temperature under the normal leaching-centrifugation regimen. The Galapagos sample and one of the MANOP splits were exposed to each leaching solution for a total of 30-45 minutes. The other MANOP sample was leached for eight hours in each solution. Both MANOP

splits started from the same seawater suspension at 2 hours after completion of the tow. The results from the Galapagos experiment are presented in Fig. III-7 and those from MANOP C in Fig. III-8. The rapid release of P, Ni, Mn, and Cd to the seawater and distilled water solutions have already been discussed for these samples. The higher percentage of these elements in the seawater from the Galapagos samples can be accounted for by their longer residence in that solution (four hours).

Several additional properties of the labile group of elements can be seen in these experiments. There are two distinct fractions - one that makes up the release to seawater and distilled water and one which is leachable by acid. There is a separation in the behavior of P and the trace cations in that the more refractory component of P is soluble only in the strongly oxidizing nitric acid solution. All the metals had a significant fraction which was solubilized, along with the Ca, by 0.1N HCl. Greater than 95% of the Ni, Mn, Cd, and Ca were removed to leaching solutions before the HNO<sub>3</sub> leach.

There was some time dependence of the elemental release to these solutions which is seen in the MANOP C experiment (Fig. III-8). This was especially significant for P, Mn, and Ni. These elements moved from the acid-solubilized pool into that solubilized by distilled water: this transformation was largely completed within 8 hours. The unbuffered 10<sup>-3</sup> N HCl solution was quickly neutralized by the CaCO<sub>3</sub> in the samples so that it should have behaved similarly to the distilled-water leach preceding it. Given this assumption, the low levels of elements in this solution in all experiments indicate that the initial

Figure III-7. Acid leaching series; Galapagos, tow 3.

Key:

The points plotted on the graph represent the % of the total particulate element released to the solution corresponding to the index number on the graph:

Horizontal index	Leaching solution
1	Seawater supernate
2	Distilled water
3	$10^{-3}$ N HCL
4	0.1N HCL
5	16N HNO <sub>3</sub>
6	Particulate residue



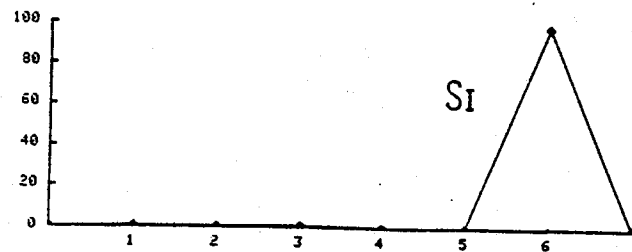
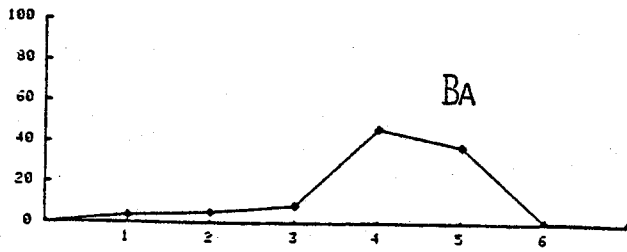
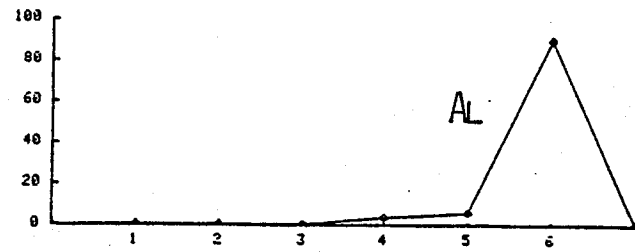
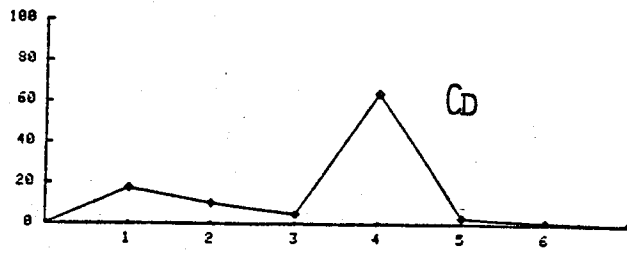
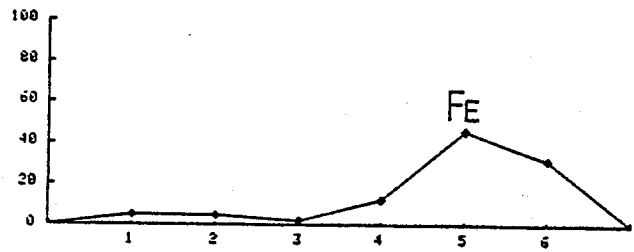
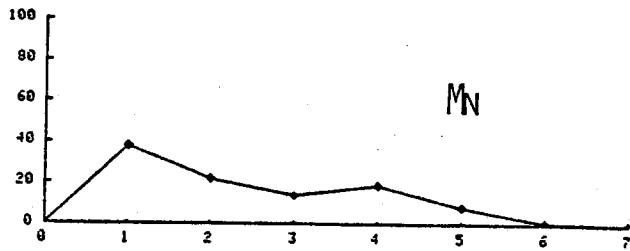
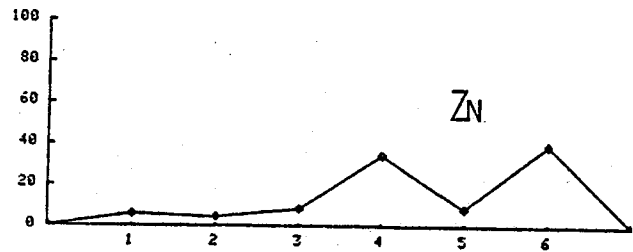
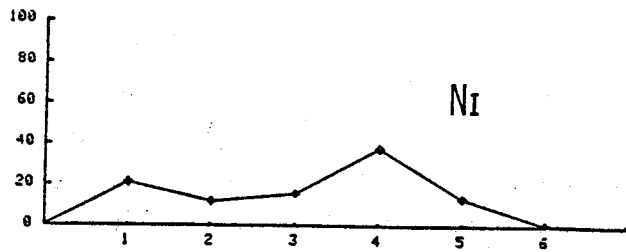
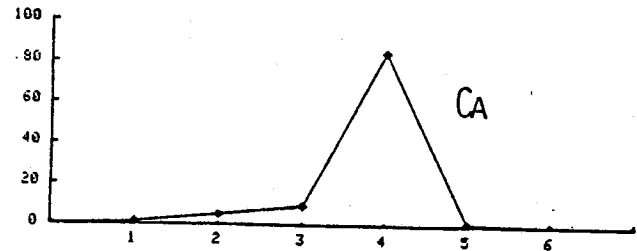
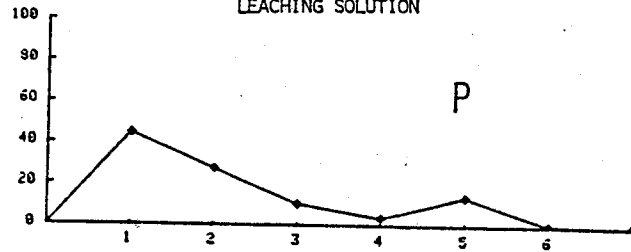
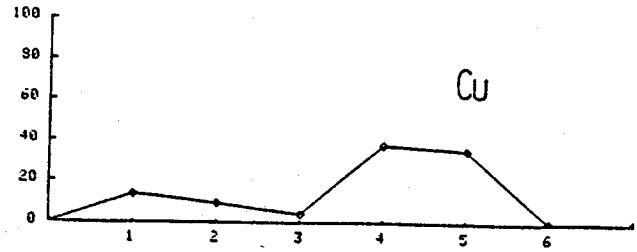
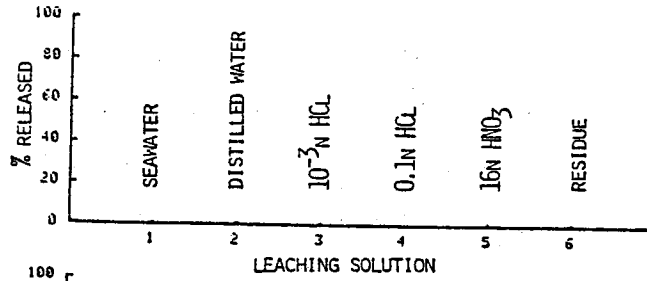


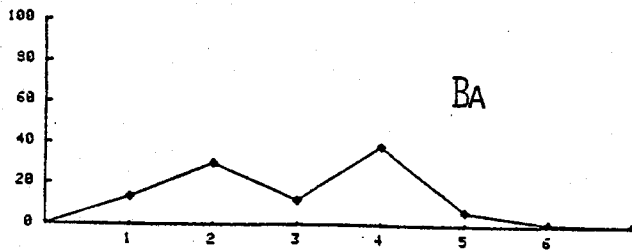
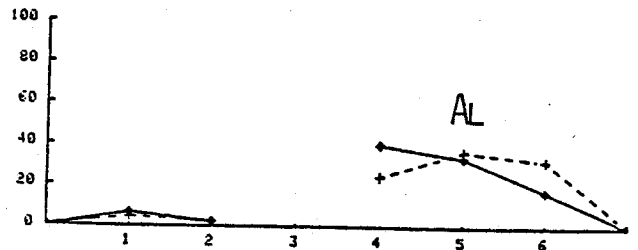
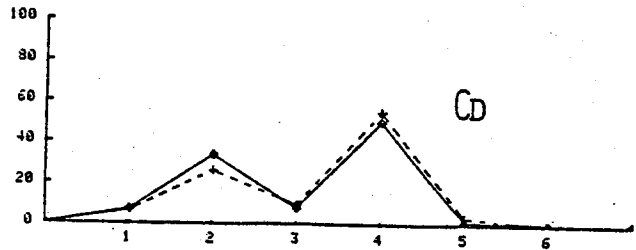
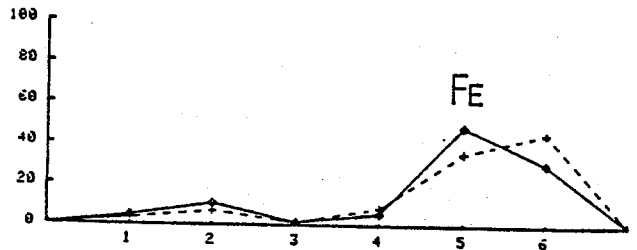
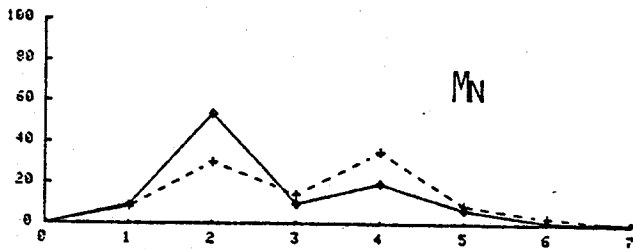
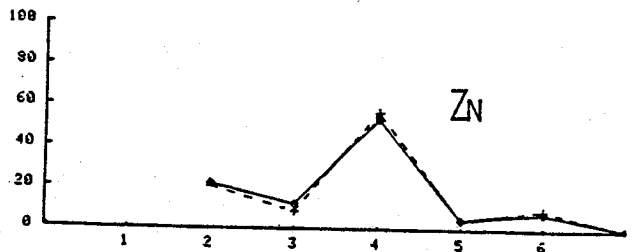
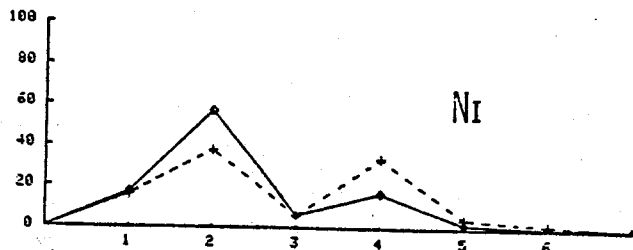
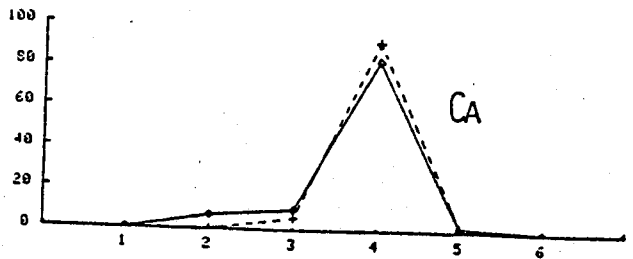
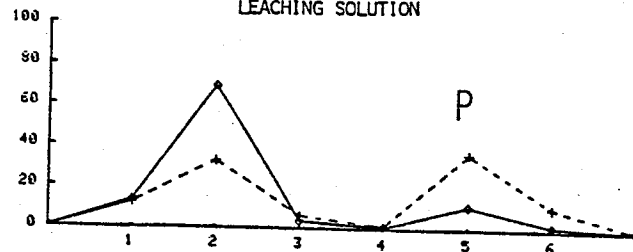
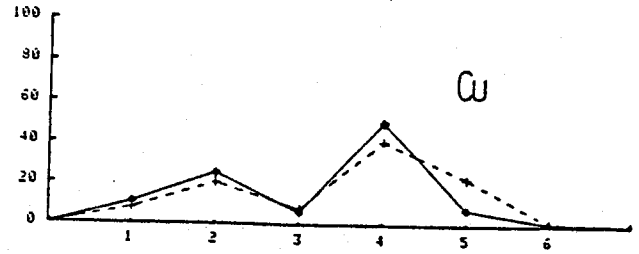
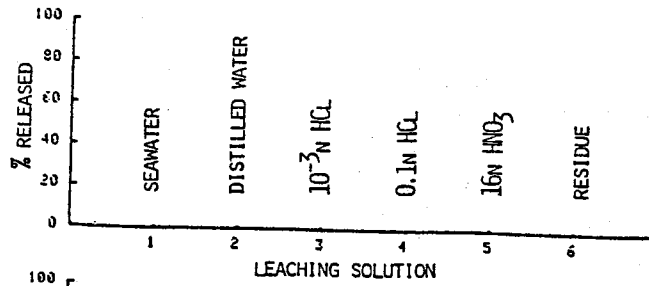
Figure III-8. Acid leaching series; MANOP C, tow 2.

Key:

The points plotted on the graph represent the % of the total particulate element released to the solution corresponding to the index number on the graph:

Horizontal index	Leaching solution
1	Seawater supernate
2	Distilled water
3	$10^{-3}$ N HCl
4	0.1N HCl
5	16N HNO <sub>3</sub>
6	Particulate residue

- Dotted line with (+) - normal short-term leaches (T43).
- Solid line with ( ) - 8 hour exposure to each solution (T44).



rapid release to distilled water is largely completed during the short leaching period, and that the transfer from the acid to distilled water-leachable pool is completed within the 8-hour suspension in distilled water.

The extraction of Cu, Ni, Cd, Ba, Mn, and Zn by the 0.1N HCl, along with Ca, is striking and suggests a possible association with  $\text{CaCO}_3$ . Lacking any direct carbonate analyses, it is assumed that a majority of the Ca released was present as  $\text{CaCO}_3$ . This is consistent with the organism distributions in the tows and with the chemical behavior of the Ca. To examine the known calcium carbonate phases in the plankton tows, single foraminifera were picked by hand, under a microscope, from the MANOP filters. The surfaces of the organisms were very carefully cleaned with a series of peroxide washes, a reductive-complexing solution, and several more distilled water washes. Occasional ultrasonification was used throughout the procedure. The forams were then dissolved in distilled water under a  $\text{CO}_2$  atmosphere. The metal/Ca ratios in this solution and in the bulk-plankton HCl leach are compared in Table III-15. All of the ratios are two orders of magnitude greater in the acid release solution than in the pure carbonate from the same samples. Although these metals are solubilized along with the  $\text{CaCO}_3$ , they are not within the carbonate matrix itself. Because of the lack of a direct carbonate analysis on these samples, it is difficult to eliminate the possibility that the released Ca was not in  $\text{CaCO}_3$  but rather in the same organic binding sites occupied by the divalent trace metals.

Table III-15. Metal/Ca Ratios

Samples :X169 MANOP C, Tow 2, 0.1N HCl, 8 hour exposure.  
Foram sample "A" - hand picked from MANOP samples.

Ratios to Ca (x10 <sup>-6</sup> )	Cu	Ni	Cd	Fe	Mn	Zn	Al	Ba
X169	63	32	60	51	15	270	270	100
Forams	.31	.4	.025	(0)	.4	.5	3.5	3

Water column "regeneration" ratios (x 10<sup>-6</sup>):

Ni/Ca - 130

Zn/Ca - 100

Ba/Ca - 1000

The last empirical partition of elements defined by the acid leaching experiments is that which contains a very refractory component which is only partly released by  $\text{HNO}_3$  or remains in the residual particles after leaching. Essentially all of the Si, much of the Fe, and variable but significant amounts of the Al and Zn resist even the 8-hour  $\text{HNO}_3$  leaching. This fraction contains very refractory organic matter, opaline skeletal material, and any included aluminosilicates. Variations in the percentage release of Al between the Galapagos sample (Fig. III-7) and the MANOP sample (Fig. III-8) must be examined in terms of the total amount of Al in each sample. The mass of Al released to the HCl solution, normalized to the mass of the plankton, was nearly identical in both samples. However, the total Al in the Galapagos sample was more than an order of magnitude greater than that in the MANOP sample suggesting the existence of two separate carriers of this element - both a refractory aluminosilicate and a more labile biogenic phase.

Compared to the more labile metals, the extremely refractory components are clearly in a very different type or site of association with the organic particles. It has often been suggested that the distribution of many elements in the water column is consistent with their incorporation into the opaline frustules of marine organisms. The plankton tow from the Antarctic, Station M provided an opportunity to examine the amount of trace elements included in marine biogenic silica which was fixed in an open-ocean upwelling region with generally higher concentrations of dissolved trace elements and a relatively low likelihood of lithogenous contamination. Analyses of the plankton

material collected, which was approximately 80% by weight  $\text{SiO}_2$ , are presented in Table III-16. These results are from the particulate fraction only, since no analyses were done on the Antarctic leaches. The sample T3 was an untreated subsample which had only been centrifuged to remove the suspension seawater. Sample T19, originally identical to the T3 subsample, was treated with peroxide and distilled water washes at 60 degrees (C) in the lab before analysis. Sample T26 was leached with distilled water and 0.1N HCl at sea. A fourth untreated sample split was digested in sodium carbonate and analyzed for total Si.

As in the pure calcite phase, the metals in this opal sample were very low. Only Al and Fe had significant percentages of their total concentrations remaining in the frustules after leaching with 0.1N HCl. The residual Fe and Al in the sample are in proportions which would be consistent with their presence in an aluminosilicate phase. The Zn and Ba were leached from the sample by the HCl solution. Since the exact chemical nature of any coprecipitated metals is not known, it is difficult to know if this leaching could remove metals from within the opaline structure. Even if we consider the total untreated or peroxide washed material as representing the concentrations in opal, the metal/Si ratios are still very low. The Ba/Si ratio is 1 to 2 orders of magnitude below the same elemental ratio seen in the water column.

Also included in Table III-16 are the results of Cu and Ni analyses on the Antarctic filtered subsamples from station M (filter A11). These were unwashed and would be roughly equivalent to the material in T3 - except for the lysis effects of filtration. The

Table III-16. Opal Elemental Ratios

Ratios to Si -  $\times 10^{-5}$   
to Al -  $\times 1$

Antarctic diatoms, Stn. M:

	Fe/Si	Zn/Si	Al/Si	Ba/Si	Fe/Al
T3 untreated	1.3	2.6	3.3	1.6	.38
T19 peroxide- water	0.6	1.9	2.7	1.1	.23
T26 HCl	(1.9)	.28	2.5	0.2	(.73)

Water column "regeneration" ratios ( $\times 10^{-5}$ ):

Zn/Si - 5            Ba/Si - 70

Antarctic diatom filter sample A11. Element ratios ( $\times 10^{-5}$ ):

Cu/Si - 0.38        Ni/Si - 0.13

Radiolaria (hand-picked from Pacific Eocene sediment samples):

Ba/Si -  $0.5 \times 10^{-5}$



concentrations of these two metals are also very low in this material and might have been even lower in a washed subsample.

Another opal carrier - Radiolaria - was examined for the concentration of Ba. There were insufficient quantities of separable radiolaria in the surface plankton tows, so two Pacific sediment samples were used. Clean, slightly-crushed radiolaria skeletons were separated from the samples and washed with distilled water,  $H_2O_2$ , and HCl. In all cases the Ba/Si ratio in the samples was low - basically comparable to that in the diatom frustules. The Zn/Si ratio in the acid leached Si is also an order of magnitude lower than the water column ratio (Bruland, 1980), but the untreated sample ratio is low by only a factor of 2.

Leaching experiments - Summary

A series of plankton collections and analyses have been performed to quantify the role of marine organisms in determining the geochemical cycles of trace elements. The samples, collected from a variety of environments, were analyzed for their total major and minor elemental concentrations and were subjected to a series of decomposition experiments to identify the chemical nature and sites of the element-particle association. It was shown that major fractions of the total Ni, Cd, and Mn are weakly associated with the plankton and are released back into seawater along with the rapidly recycled nutrient phosphorus. This process occurs within a very short time after collection of samples and appears to be due to a combination of active excretion, cell lysis, and bacterial decomposition of the organic matter. No direct, identifiable relationship exists between these labile trace metals and the P in the release products. The solubilized metals have major fractions which are small enough to pass through 0.4 $\mu$ m filters and are not strongly bound to non-polar, extractable organic material or photosynthetic pigments. The stability of any surface organic-metal binding is such that significant fractions of Cd, Mn, and Ni as well as smaller fractions of the Cu and Fe are exchangeable with high concentrations of ammonium ion and are chelatable by EDTA and APDC. These results indicate that the rapidly solubilized elements should contribute to the dissolved pool of these elements soon after the particulate material begins to decompose.

Significant fractions of the Cu, Ni, Cd, Ba, Mn, and Zn are bound to organic sites and are not rapidly exchanged with seawater or distilled water. Empirically, this pool of elements is rapidly extracted from the organic matrix at pH 1 (0.1N HCl) along with the release of Ca, but direct analysis of the calcium carbonate reveals that these elements are not incorporated in that phase. These binding sites release fractions of the Ni and Mn to the dissolved pool over time, but maintain their Cu complexing capacity until they are protonated or hydrolyzed in the acidic solution. It is likely that this fraction undergoes a much slower rate of release as these particles settle into the deep oceans and sediments.

Last, there is an even more refractory pool of trace elements associated with these plankton which contains high concentrations of Si, Al, Fe, and variable amounts of Zn. Examination of one of the major biogenic phases in this fraction, opal, shows that this is not the carrier for these elements. Smaller fractions of these metals behave similarly to the HCl-soluble pool and may be located in the same binding sites or as amorphous hydroxides. The higher concentrations of Al and some of the Fe are consistent with their incorporation in lithogenous material. It is not likely that these residual components are solubilized in the water column environment, and their transport to the sediment must be, essentially, a "single-pass" process.

Chapter IV

Discussion

IV-1. PARTICULATE ALUMINUM IN BIOGENIC SAMPLES

The concentration of Al was determined as an indicator of the presence and significance of lithogenous particulate matter. Al is a significant trace component and varies by more than an order of magnitude between different plankton samples. Results discussed in this section will show that, based on metal/Al ratios, aluminosilicate contributions to the trace elements in these plankton are generally insignificant. The exceptions to this are Al itself, and possibly Fe and Mn. Differences in the leaching behavior between these three elements makes it unlikely that even they are quantitatively bound in a single refractory silicate phase. The experiments demonstrate the presence of a dominant, chemically-resistant lithogenous Al and Fe carrier and revealed a trace fraction of Al that behaves similarly to several of the other labile trace elements. Variations in the concentration of refractory Al were consistent with variations in atmospheric input of lithogenic particulates and with dilution and scavenging by biogenic materials in regions of high productivity.

Terrigenous sources of Al.

The emphasis of this research was to study the effects of biogenic particulate matter on trace element geochemistry. The sampling of surface particulate matter does not necessarily provide the pure biogenic end-member, even in highly productive regions since there is usually some admixture of terrigenous materials. Examination of the average detrital composition of pelagic clay (Table IV-1.), which will

be taken as representing the lithogenous end-member, shows a relatively high enrichment in several metals over levels found in biogenic material. Since mixtures of biogenic and terrigenous material are, at best, difficult to separate mechanically or chemically, every attempt was made to sample biogenic material which was not significantly contaminated by lithogenous particles. Sampling sites were chosen for their distance from terrigenous sources and for their relatively high organic productivity.

The remoteness from land is not a sufficient criterion to establish the absence of suspended aluminosilicates. Long-range transport of these materials and their presence in the water column and sediments below remote mid-ocean areas are well documented (Ferguson et al., 1970; Brewer et al., 1980; Windom, 1975). In demonstrating the degree to which plankton samples contain a significant terrigenous contribution to their trace element composition, I will make use of two properties of aluminosilicates found in the marine environment. First, they are relatively constant in their composition, and second, they are resistant to chemical attack by acids.

The method most frequently used to identify terrigenous materials within a complex matrix involves the assumption that one of the measured elements is present only in the terrigenous carrier, and that all other terrigenous elements are present in known proportions. The most frequently used indicator of the terrigenous carrier phase is Al, but other elements, such as Sc, Ti, and Th-232, have also been used. Spencer and Sachs(1970) showed, using this model, that a silicate component becomes the dominant part of the sampled particulate metals

Table IV-1. Element/Al Ratios

For each element/Al ratio : column 1 - measured atomic ratio in sample  
 column 2 - ratio in pelagic clay  
 column 3 - maximum contribution of clay component to total element  
 in sample assuming all Al is present as clay.

Sample	Total Al um/gram	Fe/Al			Mn/Al ( $\times 10^{-2}$ )			Ni/Al ( $\times 10^{-2}$ )			Cu/Al ( $\times 10^{-2}$ )			Zn/Al ( $\times 10^{-2}$ )			V/Al ( $\times 10^{-3}$ )		
		(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
Detrital pelagic clay (1,2)	3100	.22			1.2			.03			.09			.08					1.4
Antarctic Str.M plankton, 1976	0.39	.44	51%										80	0.1%					
Galapagos 15meter LVFS, 1976	25 280				<5 13													24 3.7	5% 50%
Galapagos Tow 1 plankton	9	.54	40%		1.7	70%	2.2	1%		1.7	5%		13	0.6%					
Tow 3	7.8	.36	60%		1.2	100%	1.7	2%		2.2	4%		27	0.3%					
MANOP C Tow 1 plankton	0.72 0.94	1.8 1.3	12% 17%		13 10	9% 12%	35 23	0.1% 0.1%		17 18	0.5% 0.5%		140 68	<0.1% 0.1%					
S Tow 3 Tow 6	12.5 3.5	.59 .56	37% 39%		1.7 3.7	71% 32%	3.1 12	1.0% 0.3%		2.3 4.3	4% 2%		11 36	0.7% 0.2%					

(1) Krishnaswami(1976), Turekian and Wedephol(1961).  
 (2) Cronan(1969)

with increasing depth in a coastal marine environment. Brewer et al(1980) have studied the chemistry of particulate fluxes into sediment traps in the North Atlantic. The fluxes of Ti, K, V, La, Co, and Th-232 all correlate with the flux of Al, and inter-element ratios are close to those in crustal materials. The estimated terrigenous component accounts for 10 to 45% of the total mass flux collected by the traps. It cannot, however, be simply assumed that these elements are carried by terrigenous matter in all environments. Depending on the relative importance of terrigenous sources and biological productivity, the dominant carrier for, and chemical behavior of an element in the bulk suspended particles can change dramatically. An example of this effect is seen for particulate V. All of the North Atlantic sediment trap material collected by Brewer et al(1980) shows a constant atomic ratio of V to Al equal to  $1.8 \times 10^{-3}$ . The same ratio in pelagic clay is  $1.4 \times 10^{-3}$  - suggesting that both the V and Al flux are determined by a lithogenous component. In contrast to this behavior, the V/Al ratio in the large particles collected by large-volume filtration (LVFS) from the highly-productive Eastern Equatorial Pacific (Bishop et al., 1980; Collier, unpublished data) shows a surface ratio of  $24 \times 10^{-3}$  (Table IV-1, Fig. IV-1). The biogenic V is rapidly regenerated from the particulates in parallel to the release of P, while the Al remains. The V/Al ratio in the deeper, residual particles, drops to within a factor of two of the clay ratio.

The comparison made here between the North Atlantic and the Pacific particulate matter shows the importance of considering both terrigenous and biogenic material in the geochemical cycle of an

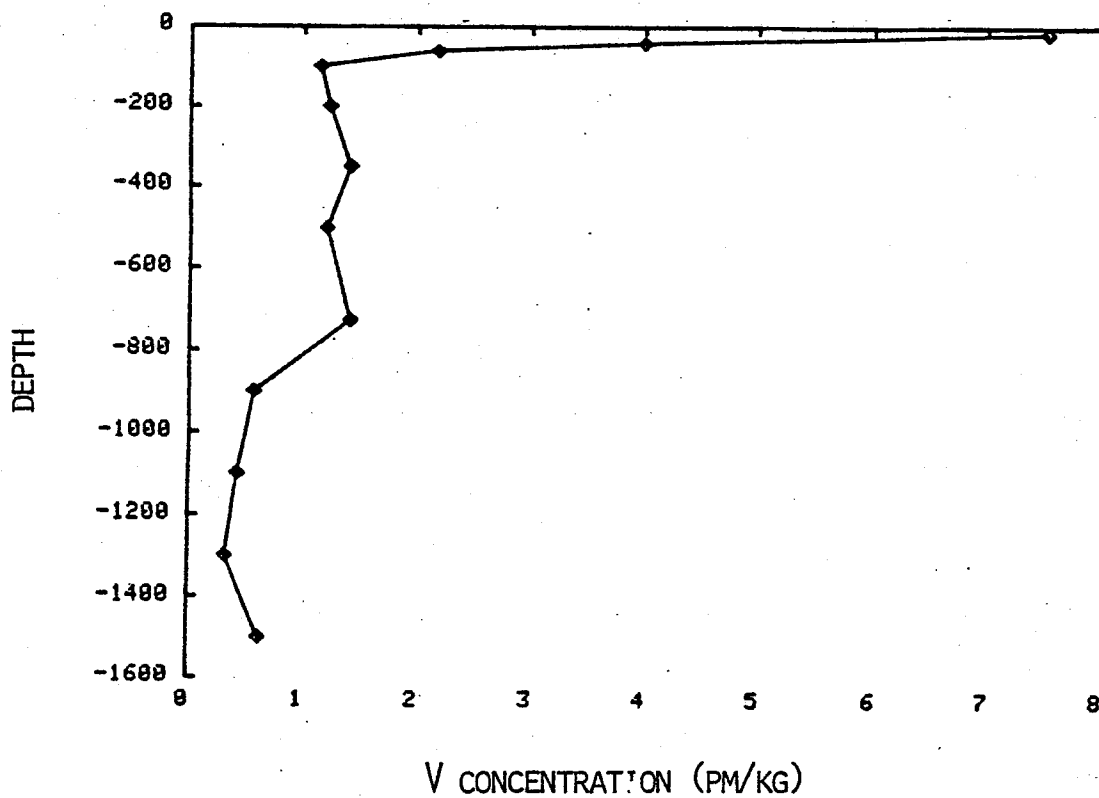


Figure IV-1. Particulate V and V/Al profile from Galapagos site.

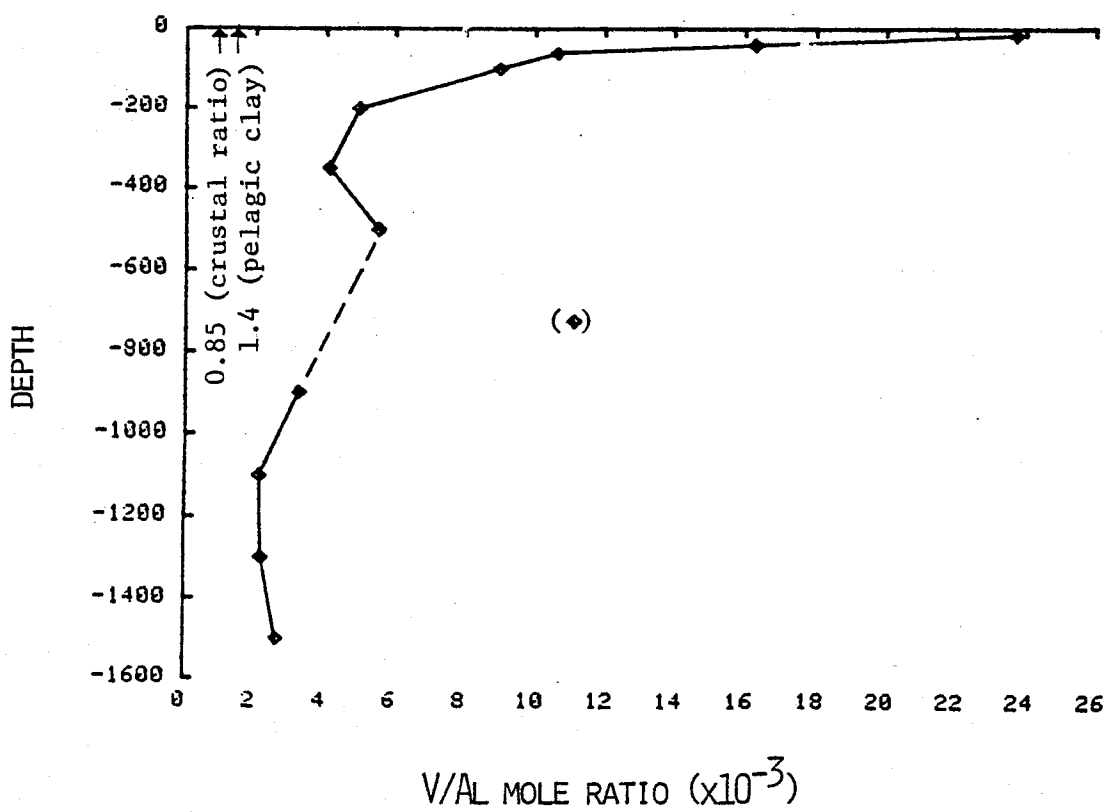
A) Particulate V vs. depth.

B) V/Al mole ratio.

A



B



element. The terrigenous fraction of a particulate element, such as Al, may dominate the total. However, it is not derived from seawater, nor does it greatly affect the dissolved concentration of that element as the particles settle through the water column. The uptake and regeneration shown for V is a completely independent geochemical process which will affect the water column distribution and the residence time of dissolved V in the oceans.

To estimate the maximum contribution of terrigenous trace elements to the plankton composition, the metal/Al ratios were calculated for each sample and compared to lithogenous metal/Al ratios (Table IV-1.) The lithogenous ratios chosen were those of Krishnaswami(1976); these are estimates of the detrital composition of pelagic clay and should represent the input composition of the lithogenous component. The end-member model assumes that all Al in suspended particles is lithogenous and present in known proportions to the other terrigenous elements. For each element, the maximum contribution of the model terrigenous component to the total measured concentration is calculated. Only Fe and Mn have concentrations in the plankton samples which could be significantly accounted for by a lithogenous component. All of the other elements have concentrations which are at least 1 to 2 orders of magnitude greater than predicted from the metal/Al ratio.

The acid leaching experiments performed on the Galapagos plankton tows (Fig. III-7, Table IV-2) showed that the relatively high concentration of Al in that sample was resistant to acid leaching. In low-temperature, short-term acid leaching experiments with sedimentary clay, it has been shown that very little of the Al (<10%) is extracted

Table IV-2. Acid Leaching Series - Results for Al, Fe, and Mn

Percentage of total particulate element released to each solution.

Sample	Total Al	Element	Leaching solutions:				
			S.W.	Dist.W.	HCl	HNO3	Residual
Galapagos Tow 3	7.8 $\mu\text{m}/\text{gram}$	Al	0.2%	0.2	4	6	90*
		Fe	5	4	14	46	32
		Mn	41	16	35	9	0
MANOP C Tow 2 8-hour exposure	0.75 $\mu\text{m}/\text{gram}$	Al	5	2	40	34	19
		Fe	3	10	7	48	32
		Mn	9	54	29	7	1

\* Concentrations in this Galapagos residual were estimated by difference between filter totals and the sums of the leaches.

by 0.5N HCl (Chester and Hughes, 1967; Agemian and Chau, 1976). Also, a significant fraction of the Mn resists acid leaching. Although the ratio of Mn/Al in the plankton is of the same order of magnitude as that reported for lithogenous material, its behavior during leaching is totally inconsistent with its presence in a refractory silicate. From 40 to 60% of the total particulate Mn was always released to the seawater and distilled water solutions, and most of the rest was solubilized in 0.1N HCl. The absence of refractory Mn in the plankton seems to conflict with the assumption that all of the Al is in terrigenous material with a known Mn/Al ratio. However, there is an increasing body of data which questions the refractory nature of the atmospheric input of Mn. Water column profiles of Mn (Klinkhammer and Bender, 1980; Jones and Murray, 1980) show a surface maximum in total Mn which is mostly accounted for in the dissolved fraction. This requires some amount of dissolution of Mn from the atmospherically-transported particulate input. Hodge et al (1978) have shown that 50% of the Mn filtered from air samples at a coastal site was solubilized when suspended in seawater even though the particulate matter possessed a crustal Mn/Al ratio. Clearly, more work needs to be done on the nature of the lithogenous particulate Mn inputs. The labile behavior of Mn in the plankton rules out its association with an aluminosilicate.

The slow solubilization of Fe from these samples by  $\text{HNO}_3$  is consistent with its presence in a silicate carrier. Samples with high particulate Al (Galapagos tows and MANOP S, tow 3) also have high particulate iron although the converse relationship is not always true.

The total Al concentration in surface particulate material has been shown to covary with the inferred rate of atmospheric input of crustal material (Krishnaswami and Sarin, 1976, 1980). The variations in Al concentrations seen in the plankton samples from this study are consistent with this distribution. In regions of high biological productivity, the terrigenous component will be further diluted by the biogenic particles and more rapidly scavenged from the surface via incorporation in and settling of fecal material and large organic aggregates (Bishop et al., 1977; Honjo, 1980). No direct measurements of clay deposition rates are available for any of the plankton sampling regions, so inferences must be drawn from the meteorological, oceanographic, and sedimentary descriptions of the areas. The Galapagos samples (plankton tows and LVFS filters) have the highest Al concentrations and were collected relatively close to the American continents. This region has been shown to have sediment compositions reflecting aeolian transport of quartz by the south-east trades (Molina Cruz and Price, 1975). Surface waters are partly composed of water upwelled at the coast of Peru (Wyrтки, 1966), and could possibly carry some amount of fine terrigenous material. The LVFS samples were collected at a time of relatively low surface productivity (Bishop et al., 1980), such that the high Al concentrations may also reflect lower dilution by biogenic material. The plankton tows were collected at the same site, ten months later, when the productivity was higher. The particulate Al was lower in these than in the LVFS samples. A variation in the aeolian transport of terrigenous components between these times is also possible (Wyrтки and Meyers, 1975).

The MANOP sites are significantly further away from land and the samples show lower levels of particulate Al. Difference in the Al between the two sites can be understood in terms of their relative productivity and the trajectories and intensities of winds over them. The mean annual productivity at site C is estimated to be on the order of  $250 \text{ mg C/m}^2/\text{day}$  (Koblentz-Mishke et al., 1970), which is similar to that at the Galapagos station during the time of LVFS sampling (Bishop et al., 1980). At site S the estimate is  $<100 \text{ mg C/m}^2/\text{day}$  (El-Sayed and Taguchi, 1979) and may be lower due to the weakening of the front between the Countercurrent and the North Equatorial Current. The surface water concentration of biogenic material was much higher at site C than at S based on the plankton yield per unit towing time.

In June, when the samples were collected, the north-east trades at site S were well developed and could carry dust from the arid regions of North America. The south-east trades over site C were much weaker and show a much longer trajectory back to a terrigenous source. The winds over the two sites are normally separated by the intertropical convergence zone (ITCZ, Wyrтки and Meyers, 1975). Silker (1972) has shown that Be-7 concentrations in the Central Pacific surface waters are more than an order of magnitude higher at  $10^\circ \text{ N}$  than at the equator. This was attributed to equatorial upwelling of older water and a much higher aerosol washout at, and north of, the intertropical convergence zone. This process could further increase the deposition flux of particulate Al at the northern site.

Site S lies at a latitude which experiences short-term and seasonal variations in surface currents and winds (Halpern, 1979). The

front between the Equatorial Countercurrent and the North Equatorial Current moves through this zone as does the ITCZ (Wyrтки and Meyers, 1975). Two tows collected at site S showed significant differences in the total concentration of Al and Fe which could be associated with variations in the atmospheric delivery of terrigenous materials to the surface waters in this region. Tows 3 and 6, which contained 12 and 3  $\mu\text{mole Al/gram}$ , respectively, were separated by 6 days of high wind and rain - possibly indicating the passage of a frontal system. Surface hydrocasts taken before tow 3 and after tow 6 showed significant intensification in the shoaler portion (125 meters) of the double oxygen minimum seen at this station. This feature is variable and its origin is not certain, however, it is thought to be an expression of horizontal mixing between the Countercurrent and the North Equatorial Current (Tsuchiya, 1968). Because both of these currents carry the same surface water mass near their interface (Wyrтки, 1967), no effects were seen in the surface water hydrographic properties. Sufficient data were not collected with the tows to document, with certainty, any change in the input of terrigenous material at site S; however, this would be consistent with the observed differences in Al concentrations, water column properties, and weather systems.

#### Non-terrigenous Particulate Al.

Based on estimates of river fluxes and dissolved concentrations in seawater, Al has a very short residence time in the oceans (100 years; Brewer, 1975). Recent analyses of Amazon river water (0.5  $\mu\text{mole Al/kg}$ ;



Stallard, 1980) and seawater (20-40 nmole Al/kg; Hydes, 1979) indicate that much of the previously compiled data were probably too high, being contaminated or including particulate Al. Removal of large amounts of the river load of Al in estuaries by a coagulation process similar to that occurring for Fe (Boyle et al., 1977a) would further lower the flux estimate. The combination of the Amazon data and Hydes's seawater values results in a calculated residence time of 1800 years. In any case, a rapid removal of the river flux ( $7-200 \text{ nmole Al/cm}^2/\text{yr}$ ) is required, implying the existence of non-lithogenous particulate Al phases. The dissolved Al profiles of Hydes (1979) display surface and bottom maxima with broad mid-depth minima. Scavenging of dissolved aluminum is indicated by curvature in the salinity - Al relationship through a region of linear potential temperature - salinity relationship. The implied dissolution of Al from the atmospheric input and the formation of new particulate phases through scavenging are both processes which, if quantitatively significant, violate the assumption that all of the particulate Al is in refractory lithogenous material.

There is no evidence or reason to suppose that Al is not taken up or scavenged by plankton. Riley and Roth (1971) were able to measure particulate Al in plankton cultured in the laboratory where the only source of Al to the cultures was dissolved contamination in the media. Martin and Knauer (1973) reported relatively large variations in the concentration of Al in their Pacific plankton samples which were consistent with those determined in this study. Significant fractions of the Al, in samples that had low total Al concentrations, were leachable into  $\text{HNO}_3$ . Although their hot-nitric reflux method would

also have removed some of the Al from clays, their results suggested that a component of the Al was carried in a more labile phase than a silicate. The distilled water - acid leaching experiments on material from MANOP C (Fig. III-8, Table IV-2) clearly show Al behavior which is different than that expected from a terrigenous carrier. This sample contained a very low concentration of total Al, 40% of which was solubilized by the 8 hour-0.1N HCl suspension and another 30% by the  $\text{HNO}_3$ . The absolute amounts of Al released by HCl from the Galapagos and MANOP samples were essentially the same and probably represent a component of Al taken up or scavenged by the organisms from Al dissolved in the seawater. To get an estimate of the magnitude and significance of the Al flux associated with this biogenic phase, we can use the HCl-solubilized Al ratio to total P in the MANOP C samples ( $\sim 1 \times 10^{-3}$ ) and the particulate P flux out of the surface ocean ( $0.87 \mu\text{mole}/\text{cm}^2/\text{yr}$ ; Froelich, 1979). The associated Al flux from the surface ocean is  $0.9 \text{ nmole}/\text{cm}^2/\text{yr}$  - only a small fraction of the river flux and insufficient to be expressed as a measurable surface depletion in dissolved Al. Unlike P, which is remineralized in the deep ocean, the Al flux should increase with depth as the particles continue to scavenge Al (Hydes, 1979).

Another possible biogenic carrier for Al is the siliceous tests of diatoms and radiolarians. The proposed associations include adsorption (Lewin, 1961; Hydes, 1979) and actual incorporation within the opaline lattice - in solid solution or as an authigenic phase (von Bennekom and van der Gaast, 1976). To test the importance of structural incorporation of Al in opal, the diatom samples from Antarctic stn. M

were analyzed (Table III-16). The concentration of Al was found to be very low ( $\text{Al/Si} = 3 \times 10^{-5}$ ), as were the concentrations of Fe, Ba, and Zn. Both the Al and the Fe were resistant to HCl leaching and the Fe/Al ratio was 0.44 - only a factor of two above the lithogenous ratio. Even at these low concentrations of Al, the carrier cannot be distinguished from terrigenous material based on element ratios. If one assumes that all of the Al is in the opal and that this Al/Si ratio is representative of all biogenic silica then an annual deposition of biogenic  $\text{SiO}_2$  of  $4 \times 10^{14}$  g/year (Demaster, 1979) produces an Al deposition of  $2 \times 10^8$  moles /year. This flux is two orders of magnitude lower than the lowest estimated river flux and shows the insignificance of this carrier in the overall cycle of dissolved Al.

#### Conclusions.

- 1) Based on the acid resistant behavior of Al in these plankton samples, terrigenous material was shown to be present at low and variable levels. Variations in the Al content of the plankton were consistent with delivery rates of lithogenous material and its dilution by high rates of biological particulate production.
- 2) The refractory component never contributed significantly to the trace element composition of the plankton except for Al and some of the Fe.
- 3) A labile fraction of the Al was identified which was significant in samples that had very low levels of terrigenous material. This fraction results in a flux of Al out of the mixed layer which may be of

the same order of magnitude as the river flux of dissolved Al.

4) Opal was examined as a possible carrier of Al. The concentration of Al in Antarctic diatom samples was shown to be very low compared to other plankton samples and still not distinguishable from a terrigenous component based on its Fe/Al ratio. The flux of Al to the sediments in this carrier is at least two orders of magnitude below the river input of Al.

#### IV-2. BIOGENIC TRACE ELEMENT CARRIERS

In this section I will discuss the biogenic carriers of the trace elements as inferred from the results of the leaching experiments and from metal-carrier distributions in the marine environment.

Identification of the precise metal-organic compounds or functions in these heterogeneous, chemically unstable particulate samples is beyond the scope and intention of this investigation. The plankton leaching experiments have quantified the trace element associations with various carriers in surface-ocean particulate material. The known cycles of these carriers will be used to examine the significance of the biogenic associations in the geochemical cycles of the trace elements.

Most of the trace elements studied were associated with the non-skeletal organic phases of the particulate samples. The three basic partitions of elements defined by the leaching experiments were: extremely labile release products; the HCl-soluble fraction; and the refractory components which were only released by the nitric acid or remained in the particles throughout the experiments. These are not intended to represent concrete or mechanistic definitions but rather provide useful distinctions between the behavior of the trace elements along with their major carriers.

##### Labile Organic Associations

The dominant particulate fraction of several of the elements studied was that which was very weakly associated with the particles and covaried with P during leaching. The rapid release of P and N to

sea water by marine organisms has been documented for both zooplankton excretion (Butler et al., 1970) and decomposing phytoplankton (Grill and Richards, 1964). The loss of these elements from particles in the upper oceans has been demonstrated for suspended material (Bishop et al., 1980) and settling material collected in sediment traps (Knauer et al., 1979). Evidence from the rates of total primary production in the euphotic zone (Eppley and Peterson, 1979; King and Devol, 1979) and from the relationship of the chemical composition of phytoplankton to their growth rates and nutritional states (Goldman et al., 1979) indicates that N and P are rapidly recycled within the euphotic zone.

The experiments reported here show that a group of labile trace metals are released along with the micronutrients. Major fractions of the total Cd, Ni, and Mn are found in the sea water and distilled water leaching solutions. This is the first reported documentation of this process occurring in open-ocean biogenic particles, although it had been predicted from the water column distribution of the dissolved species (Boyle, 1976). In every experimental examination of Cd in laboratory cultures of marine organisms, its labile association with the cell contents or organic surfaces has been noted, but the nature and function of this association is not known (Cossa, 1976; Kremling et al., 1978; Sick and Baptist, 1979). Knauer and Martin (1980) have reported a significant release of both Cd and P to the hyper-saline collection fluid in a sediment trap. No specific references to such behavior for Ni or Mn have been published.

The various leaching experiments indicate that this regenerated material is derived from several different sites within the plankton

particles. Significant acceleration of the release due to osmotic shock indicates the presence of these elements in a dissolved pool within cell structures. Direct excretion by the zooplankton in the tows can account for a portion of the release products. The initial and rapid release of P is higher than reported rates of zooplankton excretion (Butler et al., 1979). This active process is accelerated by the physical shock of the plankton tow and concentration process (Hellebust, 1974).

The dissolved nature of the released trace elements was demonstrated by several other experiments. Significant fractions of the released elements are not filterable, they are not directly extractable into non-aqueous solvents, and they are in a form which is available to chelation by APDC followed by extraction of the complex into chloroform.

Increased amounts of trace metals were extracted from the particles by iso-osmotic solutions containing APDC, EDTA, and  $\text{NH}_4\text{Cl}$  indicating that a fraction of the labile elements are weakly bound to exchangeable surface sites. Also, there was a time-dependent transfer of the trace elements into the labile pool from the more refractory material. Some portion of the labile materials are in kinetically less available sites within the plankton. In EDTA-leaching experiments with plankton samples, Mopper and Degens (1972) reported the release of significant fractions of the total hydrolyzable monosaccharides and amino acids. This was attributed to the extraction of metals functioning as binding bridges between these organic ligands and other organic surface sites.

The role of bacterial activity in the observed regenerations is hard to quantify. Hellebust(1974) has noted the difficulty in separating heterotrophic bacterial activity from active excretion or autolysis and the general ineffectiveness of antibiotic treatments in stopping bacterial decomposition in collected plankton samples. However, a significant decrease in the release of P after the addition of antibiotics was noted. Because these samples became contaminated with Ni and Cu, the direct effects of antibiotics on the metal releases was not determined.

In summary, a significant fraction of the biogenic Cd, Mn, and Ni are weakly bound to surface planktonic particulate matter. This fraction is rapidly regenerated to dissolved material in the upper ocean, along with the nutrient P, through active excretion, cell lysis, and heterotrophic activity. The geochemical cycles of P, Cd, Mn, and Ni will be discussed in section IV-4 as they reflect the sites of regeneration and the significance of the release products in the total fluxes of these elements.

#### HCl-soluble material

Most of the remaining fractions of the non-silicate trace elements were solubilized by 0.1N HCl. Although  $\text{CaCO}_3$  was specifically solubilized in this solution, that phase was shown to be an insignificant carrier of the metals found in the particles. Several lines of evidence suggest that hydrous metal-oxide precipitates are unlikely to be significant carriers of these trace elements in biogenic particles. Fe is the only metal present in sufficient quantities to be



considered as a possible carrier of this type. The proposed mechanisms of uptake include surface adsorption (Murray, 1975; James and MacNaughton, 1977) and homogeneous incorporation as a solid solution within a freshly formed precipitate. Adsorption at metal oxide surfaces has been modeled as the formation of surface hydroxyl complexes with the metal or hydrated metal (James and MacNaughton, 1977). The maximum number of surface adsorbing sites in an FeOOH precipitate must be  $\leq$  the total number of moles of Fe in the precipitate. The plankton samples contain approximately 2  $\mu$ moles Fe/gram which results in 0.01  $\mu$ mole Fe/ml in the sea water-plankton suspension. The EDTA was added to the sample to make a concentration of 1.0  $\mu$ mole EDTA/ml suspension: at least 100-times more concentrated than the Fe sites. At pH 8, the formation constants for the metal-EDTA complexes are at least 10 orders of magnitude larger than those for the formation of the metal-surface complexes (Sillen and Martel, 1971; Balistrieri et al., 1980). If adsorption at the surface of a hydrous iron oxide precipitate was quantitatively important in these samples, then a larger percentage of the the metals would have been exchanged from the surfaces by the addition of EDTA.

It has been demonstrated that metal oxides and hydroxides adsorb dissolved organic material from natural waters (Davis and Leckie, 1978; Davis, 1980). If such precipitates are present in the plankton samples, they are very likely to be coated with adsorbed organic material. The metal adsorption properties of these systems take on the properties of the exposed organic ligands rather than those of the surface hydroxide groups.

The significance of a homogeneous Fe oxide with coprecipitated trace metals as a source for the HCl release products is also not likely. The ratio of metal/Fe in the bulk material is on the order of 10. The ratio seen in the HCl leaching solution is generally less than 2. While greater than 90% of the other trace elements are solubilized by the HCl, only 40-60% of the Fe is leached.

These experiments do not rule out the presence of iron precipitates. It is possible that the non-silicate Fe is, in some part, present as a well-aged Fe hydroxide phase. However, it is not likely that it serves as a significant trace element carrier in these surface-ocean organic particulate materials.

Elimination of the two mineral carriers -  $\text{CaCO}_3$  and hydrous iron oxides leaves fixed organic ligands as the likely site of metal binding for the HCl-soluble fraction. There is little surprise in this result, although the characterization of these metal complexes has hardly begun. Approximately one quarter to one third of all proteins and enzymes that have been purified contain metals or require metal ions for their biological activity (Ibers and Holm, 1980). These are generally classified into two groups: metalloproteins and metal-activated proteins or complexes (Hughes, 1972). In the first group the metal is firmly bonded as part of the structure of the protein. In the second classification the metal ion - binding group interaction is much weaker. The metalloproteins and enzymes are relatively resistant to chemical attack and are bound to the metals through multi-dentate associations at their more basic residues such as the imidazole ring of histidine and the thiol group in cysteine. These complexes are usually metal-

specific and the metals function as structural templates or redox catalysts. The metal-activated proteins and complexes are lower in stability, are less metal-specific, and can be reversibly dissociated from their metal ions by acid or prolonged exposure to low metal activities (eg., through dialysis). The metals in these systems usually function as Lewis Acids in their catalysis and their association with the donor sites usually follows the Irving-Williams order of stability for divalent cation complexes. Typical ligands involved include carboxyl, hydroxyl, and amino groups.

The solubilization of the trace elements from the plankton samples is generally consistent with the stability of metal-organic complexes. The fractions of the Cu and Fe that were released by the  $\text{HNO}_3$  solution may have been bound within stable metalloproteins. These metals have been studied in numerous enzymes involved in electron transport, oxygen transport, and storage. Zn is also functional in numerous hydrolytic enzymes. Only small fractions of the total Cu, Fe, and Zn were released to the non-acidic leaching solutions - consistent with their metalloprotein associations and with their stable organic ligand complexes. At the other extreme, the rapid release of Cd and Mn can be interpreted in terms of the low stability of their organic complexes (Hughes, 1972). A leaching result which was inconsistent with this model is the relative stability of the particulate Ba phase. In general, due to its very large ionic radius, Ba forms very weak organic complexes.

It has been shown that a large fraction of most of the particulate trace elements studied here are either dissolved in cell fluids,

loosely bound to organic surfaces, or more specifically associated with metalloproteins and complexes. A precise knowledge of the regenerative behavior and transport of these metals will require specific knowledge of the binding sites and the fate of the organic matter involved. Although we are still a long way from both of these goals, having established the ratios of the trace elements to major elements representing the carriers allows the examination of the element cycles in the water column and sediments.

#### Refractory Carriers

The total fraction of any trace element which was not solubilized by the leaching solutions was generally small. The exceptions were Fe and Al - the residual components of which have already been discussed in terms of terrigenous materials scavenged by the biogenic particles.

Variable amounts of Cu, Fe, P, Mn, and Zn are resistant to acid leaching and are probably associated with more refractory metalloproteins and storage products. The degree of solubilization of this resistant fraction in  $\text{HNO}_3$  is time dependent. This suggests the progressive exposure of sites which, due to the physical structure of the organism or some other kinetic limit, are not in immediate contact with the leaching solutions.

The primary form of Si in the samples, biogenic opal, is not soluble in the leaching solutions. It was shown that this phase was not a significant carrier for any of the elements studied except, possibly, for Zn. The Zn/Si ratio in the residual fraction of MANOP tow 2 was approximately  $10^{-4}$ . The ratio measured in both unwashed and

acid leached diatoms was lower -  $10^{-5}$ . The water column ratio is approximately  $5 \times 10^{-5}$  (Bruland, 1980), indicating that the refractory opal carrier could, in part, account for the Zn transport.

IV-3. SURFACE WATER PROPERTIES AND BIOGENIC PARTICULATE ELEMENTS.

Several models will be discussed in an attempt to quantify relationships between the total particulate element concentrations and environmental factors such as the dissolved concentrations of nutrients and trace elements. Two questions can be asked: 1) How is the uptake of trace elements and nutrients by organisms expressed in the dissolved concentrations of those elements in the surface waters? 2) To what degree does the surface environment determine the composition of the biogenic particulate matter? The data presented in this study, or in the rest of the literature, do not yet uniquely answer these questions, which are asked by geochemists and plankton ecologists, alike. However, it will be demonstrated that significant progress has been made on several parts of their resolution.

One of the first systematic trends seen in the total-concentration data was in the Antarctic samples where a distinct decrease in the total particulate trace element concentrations was seen in samples from increasingly nutrient-rich environments. This occurred even though the nutrient increase was accompanied by the parallel increase in upwelled trace elements. Knauer and Martin(1973) have also noted a decrease in the concentrations of Cd in plankton during bloom conditions compared to those at other seasons in a coastal environment. These observations are consistent with a model for Si uptake by diatoms in laboratory cultures proposed by Rueter(1979). In these systems, Zn was shown to be involved in the uptake mechanism for  $\text{Si(OH)}_4$ . Toxicity of Cu seemed to function through a blockage of the proposed metalloenzyme site

through competitive binding, resulting in the transport of Cu into the cell. This effect was partially overcome by increasing the concentrations of either Si or Zn which both caused a decrease in the Cu associated with the cell. These culture systems can be compared to the Antarctic upwelling system where there is an increase in dissolved Si and presumably Zn (Bruland, 1980). At low dissolved activities of nutrients, the competitive-binding model predicts that there are more sites available for Cu (and possibly other metals). A change in the nature of the surface binding sites between a eutrophic and oligotrophic metabolism could also explain the higher percentage of Cd rapidly released to sea water by the plankton samples from the Galapagos compared to the MANOP S samples. More work needs to be done in upwelling systems and in cultures to explain these observations.

Environmental control of planktonic trace element compositions.

In discussing the relationship between biogenic particulate matter and the dissolved elements in sea water, it is useful to consider two classifications of trace elements based on their water column distributions. The first group consists of those elements which are essentially depleted to zero in the surface water, with respect to their deep water concentrations. This group includes the nutrient elements N, P, and Si, and the trace elements Cd and Zn. These elements are equivalent in distribution to the "bio-limiting" elements defined by Broecker (1974). However, in grouping these elements together, it is not suggested that the trace elements are necessarily involved in the nutrient status or growth limitation of the organisms.

The other classification of elements includes those which are taken up by the organisms but which show only partial surface depletions with significant residual concentrations. This group is equivalent to Broecker's(1974) "bio-intermediate" classification and includes Cu, Ni, Mn, and Ba.

Systematics of the trace element-nutrient relationships will be examined in terms of the element ratios to a "bio-limiting" nutrient element, P. It is assumed that the total biogenic flux of a trace element out of the upper ocean can be expressed in terms of an initial ratio to P and the total rate of production of biogenic particulate material. This makes no assumptions about a functional relationship between these elements (other than their association with the planktonic particles), nor any assumptions about the regenerative fractionation of the particulate elements.

Boyle et al.(1980) have investigated variations in the horizontal distributions of surface Cu, Ni, and  $PO_4$  in terms of inferred ratios in biogenic particles formed in the mixed layer. The ratio in the particles is compared to that in the surface water:

$$\alpha = \frac{(\text{metal/P})_{\text{plankton}}}{(\text{metal/P})_{\text{water}}}$$

The authors also allowed for the rapid regeneration of nutrients and trace elements within the upper waters, such that the settling material could have a different ratio described by:



$$\beta = \frac{(\text{metal/P})_{\text{sinking}}}{(\text{metal/P})_{\text{plankton}}}$$

As long as this regeneration is taking place within the mixed layer, the product of the ratios,  $\alpha \cdot \beta$ , compares the relative enrichment or depletion of the particulate trace elements with respect to the dissolved ratios. In the statement of these two ratios,  $\alpha$  and  $\beta$ , it is not intended to imply that they are constant in time or space. In fact, it will be demonstrated that they do vary. However, the ratios are useful in characterizing the flux of materials out of the mixed layer without independent knowledge of the absolute magnitude of each elemental flux.

The total concentration data for the Pacific plankton samples are presented in Table IV-3 in terms of these various ratios. The relative sea water release percentages from the leaching experiments are used as first-order estimates of the magnitude of  $\beta$ . The percentage of the total trace element not released to the sea water suspension is divided by the same percentage for P. These estimates could be subject to large errors since the relationship between rapid regeneration in the upper ocean and the sea water suspension experiment is not known. The relative importance of active excretion, bacterial activity, autolysis, and zooplankton grazing in contributing to a net value of  $\beta$  has not been quantified. The geochemical mass balances for these trace elements, discussed in section IV-4, generally support the values of  $\beta$  in Table IV-3 chosen for the "bio-intermediate" trace elements but predict a lower value for Cd ( $\beta < 1$ ).

Table IV-3. Total concentration ratios.

Sites:		G	C	S		G	C	S	
	Cd	.10	.38	.37		.89	.55	.66	
Surface Water Ratios to P  (x10 <sup>-3</sup> )	Zn*	.35	2.4	3.0	Plankton Ratios to P  (x10 <sup>-3</sup> )	5	3	3.3	
	Cu	2.6	17	28		.56	.52	.54	
	Ni	3.7	58	72		.58	.86	1.1	
	Mn*	3.8	29	52		.40	.34	.42	
	Ba*	45	830	1300		1.2	1.7		
<hr/>					<hr/>				
	Cd	9	1.5	1.8		1.6	1.6	3.0	
Ratio of Plankton to Water Ratios  ( α )	Zn	14	1.3	1.1	Relative Seawater Release Ratio  ( β )	6			
	Cu	.22	.03	.02			3.4		
	Ni	.16	.01	.02			2.4		
	Mn	.11	.01	.01			2		
	Ba	.03	.002				6		

Sites: G - Galapagos  
C - MANOP C  
S - MANOP S

\* Estimated surface water dissolved concentrations from:  
Zn - Bruland(1980); Mn - Klinkhammer and Bender(1980);  
Ba - GEOSECS Pacific, Edmond(personal communication)

Several features of the data in Table IV-3 clearly relate to possible uptake models for the trace elements. Because the concentrations of "bio-limiting" elements all decrease from elevated concentrations in upwelling regions to nearly zero in oligotrophic waters, the ratios between them remain relatively constant. However, the ratios between the "bio-intermediate" elements and P show a large range - up to very high values in oligotrophic waters due to the disappearance of P. In contrast to these variations in the dissolved ratios, the same ratios in the plankton samples are much more constant and show very little relationship to the dissolved variations. A conclusion can be drawn that these plankton trace-elemental concentrations are not determined in simple linear proportion to the water column ratios. This emphasizes the relatively specific nature of the organic association of these trace elements. In a broad sense, this observation can be compared to the major-element plankton compositions, or "Redfield ratios", which are relatively constant in marine plankton compared to large variations in the ratios of dissolved inorganic C, N, and P.

Another important property of the ratios presented in Table IV-3 is that the values of  $\alpha$  (or  $\alpha \cdot \beta$ ) for the "bio-limiting" elements are always  $\geq 1$ , demonstrating the particulate enrichment driving the depletion of these elements from surface water as fast as or faster than that of P. In a consistent manner, the elements with residual surface concentrations show values of  $\alpha$  (or  $\alpha \cdot \beta$ ) which are less than 1.

Based on these data, it is clear that the trace element composition of the plankton is controlled by more complicated processes

than a simple, direct proportionality to the dissolved concentrations. This is not to say that there is not any relationship. Indeed the increase in the Ni/P ratio in the Pacific plankton may be a response to the much greater increase in that ratio in the surface water. However, the general insensitivity to these changes and the decrease seen in Cu and other particulate metals in highly productive waters indicate a more complicated dependence on the metabolic uptake sites.

Horizontal distributions of dissolved trace elements.

A significant fraction of the total marine primary production occurs in regions where deep water is upwelled to the surface and in transition zones between these regions and the oligotrophic central gyres (Koblentz-Mishke et al., 1970). These regions appear especially important in providing the flux of "newly produced" organic material to the deep oceans in view of the lower percentage of internal recycling of nutrients which sustain the high levels of total production (Epply and Petersen, 1979). These environments must also be important in transporting a large fraction of the biologically cycled and scavenged trace elements due to the higher biogenic particulate fluxes generated. The characteristic enrichments of the co-varying nutrients and trace elements in these regions have been discussed (Antarctic transect from this study; Boyle and Edmond, 1975; Bruland, 1980; Boyle et al, 1980). If the evolution of the upwelled water could be considered a closed system, except for the production and settling of biogenic particulate matter, then tracing the progression of the nutrient and trace element depletions would yield information on the uptake kinetics and

composition of the particulate matter produced. This is analogous to the study of laboratory cultures: a combination of a closed batch system with no new nutrient inputs (Droop, 1975), and a continuous culture where the produced particulate material is removed from the system via the outflow (Droop, 1974). The change in dissolved concentrations over the horizontal extent of the system (seen as a time frame of evolution) must be equal to the particulate flux out of the volume. Ratios of these changes between dissolved trace elements and P should express the ratios in the particles. Boyle et al. (1980) have applied this model to the dissolved surface distributions in the North Pacific published by Bruland (1980). The inferred particulate compositions will be compared to those determined in this study although they were collected from different parts of the Pacific. A more thorough analysis will require plankton and water samples collected from the same regions.

Dividing the dissolved metal-vs- $PO_4$  plots into three consecutive linear sections and taking the slope over each section gives the predicted elemental ratios for the particles causing the depletion (Table IV-4). For Cu and Ni, the ratios are relatively constant but significantly higher than those measured in the surface plankton. Fig. IV-2 summarizes the total particulate metal/ $PO_4$  relations for Cu, Ni, and Mn as determined in the Pacific plankton samples. Applying the relative sea water release ratios for these metals and P as an indicator of  $\beta$ , gives an estimate of the settling particle flux ratio which is within the range of the dissolved slopes. If these data are representative of the particles produced in the more northern

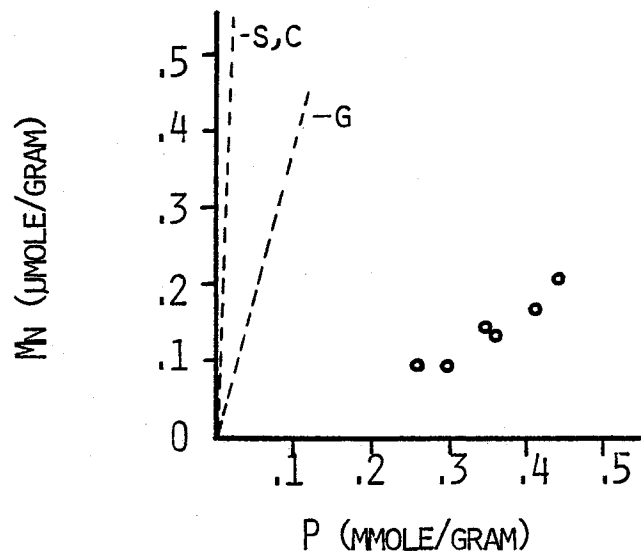
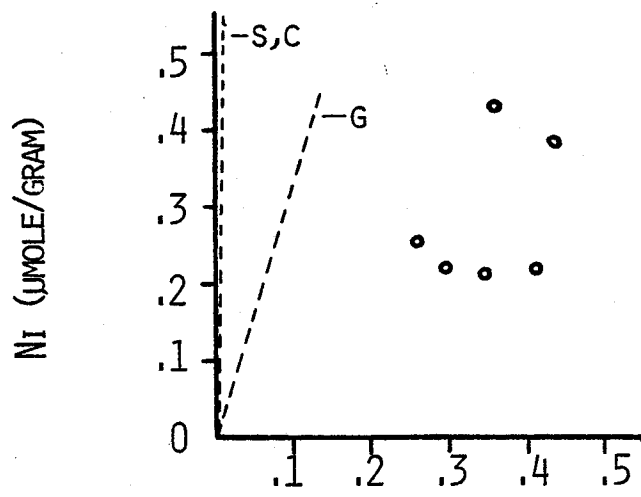
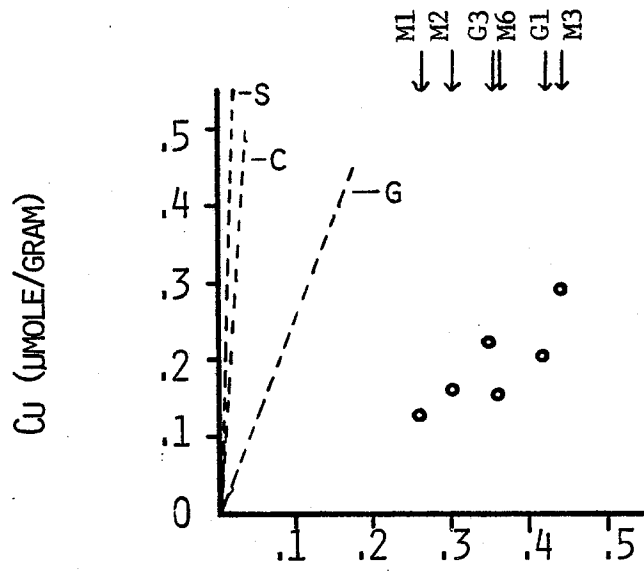
Table IV-4 Surface water depletion vs. plankton ratios. ( $\times 10^{-3}$ )

	$\Delta \text{Cu} / \Delta \text{P}$	$\Delta \text{Ni} / \Delta \text{P}$
North Pacific surface transect (Bruland, 1980)		
Stations 13 - 18	1.9	3.2
17 - 21	1.4	2.4
20 - 25	2.2	8
	Cu/P	Ni/P
Pacific plankton ratios (this work)	0.54	0.6-1.1
(ratios) x ( $\beta$ )	1.8	0.7-2.6
( $\beta$ ) used from table IV-3: Cu = 3.4 Ni = 2.4		

Figure IV-2. Total plankton compositions: Cu, Ni, Mn, vs. P.

Sample key: G1 - Galapagos tow 1.  
G3 - Galapagos tow 3.  
M1 - MANOP C tow 1.  
M2 - MANOP C tow 2.  
M3 - MANOP S tow 3.  
M6 - MANOP S tow 6.

(Dotted lines are surface water dissolved ratios at each site.)





environment, then the ratios measured in the surface plankton samples appear to represent unfractionated material and not the settling composition.

When this surface analysis is applied to a "bio-limiting" element, Cd, several difficulties arise. The Cd and P relationship from the Bruland(1980) surface samples are shown in Fig.IV-3. The slope of the  $\Delta \text{Cd} / \Delta \text{P}$  relationship in the surface transect is not at all constant. The Pacific vertical profile data frequently show that Cd is depleted before P in near-surface waters (Boyle et al.,1976; Appendix I). However, caution must be used in applying this generality since Boyle et al.(1980) have detected higher Cd values in other regions of the surface Pacific. The particulate Cd in the organisms could account for some of these differences - 100 ug/kg total particulate mass concentration with a plankton composition of 300 nmole/g Cd contributes a very significant 30 pmoles/kg to the total surface water inventory (note that data plotted in Fig. IV-3 were from filtered samples).

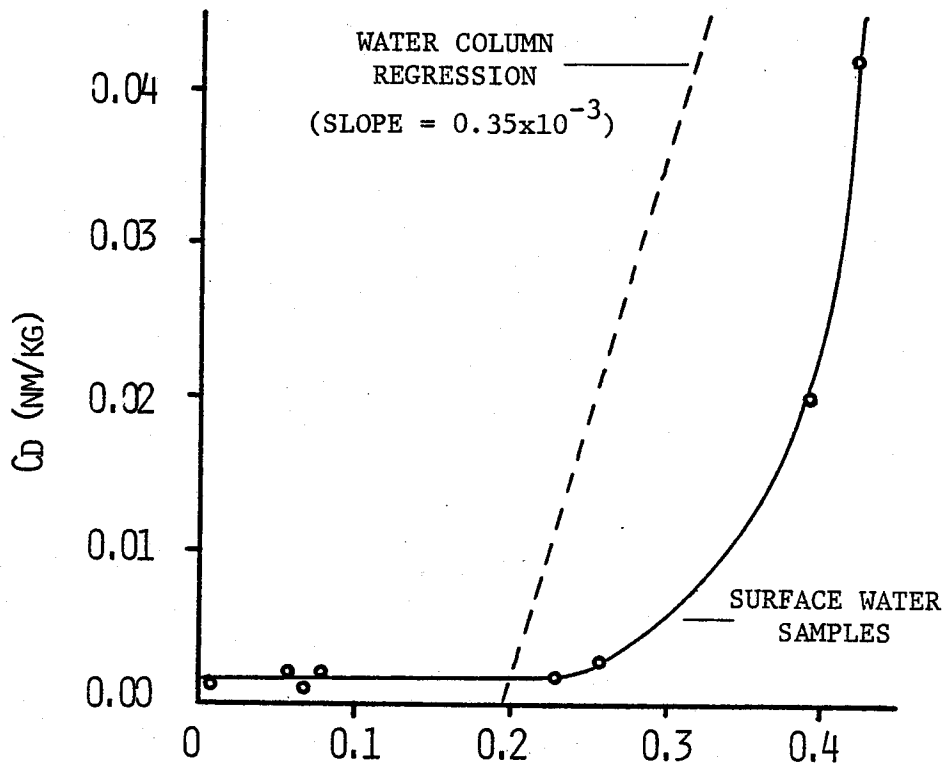
After the dissolved Cd concentration has been depressed to near the detection limit, the concentration of  $\text{PO}_4$  continues to decrease - implying a flux of relatively Cd-poor particles out of the nutrient-depleted waters. This distribution (Fig. IV-3), coupled with the model describing particulate ratios, predicts widely varying particulate Cd/P ratios which are initially very high and drop off to very low values in oligotrophic waters. These low ratios, required by the application of the horizontal model to these oligotrophic waters, either exist, and have not yet been sampled, or the model has not described the system. All of the plankton analyses for Cd and P from this study and those of

Figure IV-3. Cd-P systematics: surface distributions, uptake ratios, and plankton compositions.

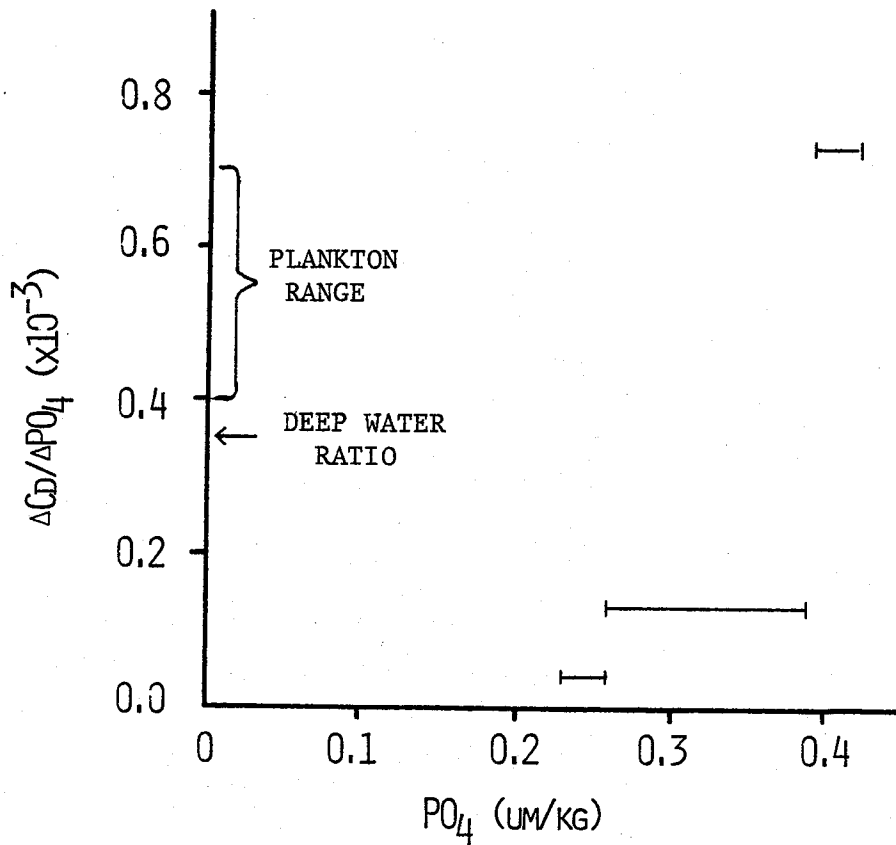
A) Dissolved Cd vs.  $PO_4$  (Bruland, 1980).

B)  $\Delta Cd / \Delta PO_4$  between stations plotted in A.

A



B



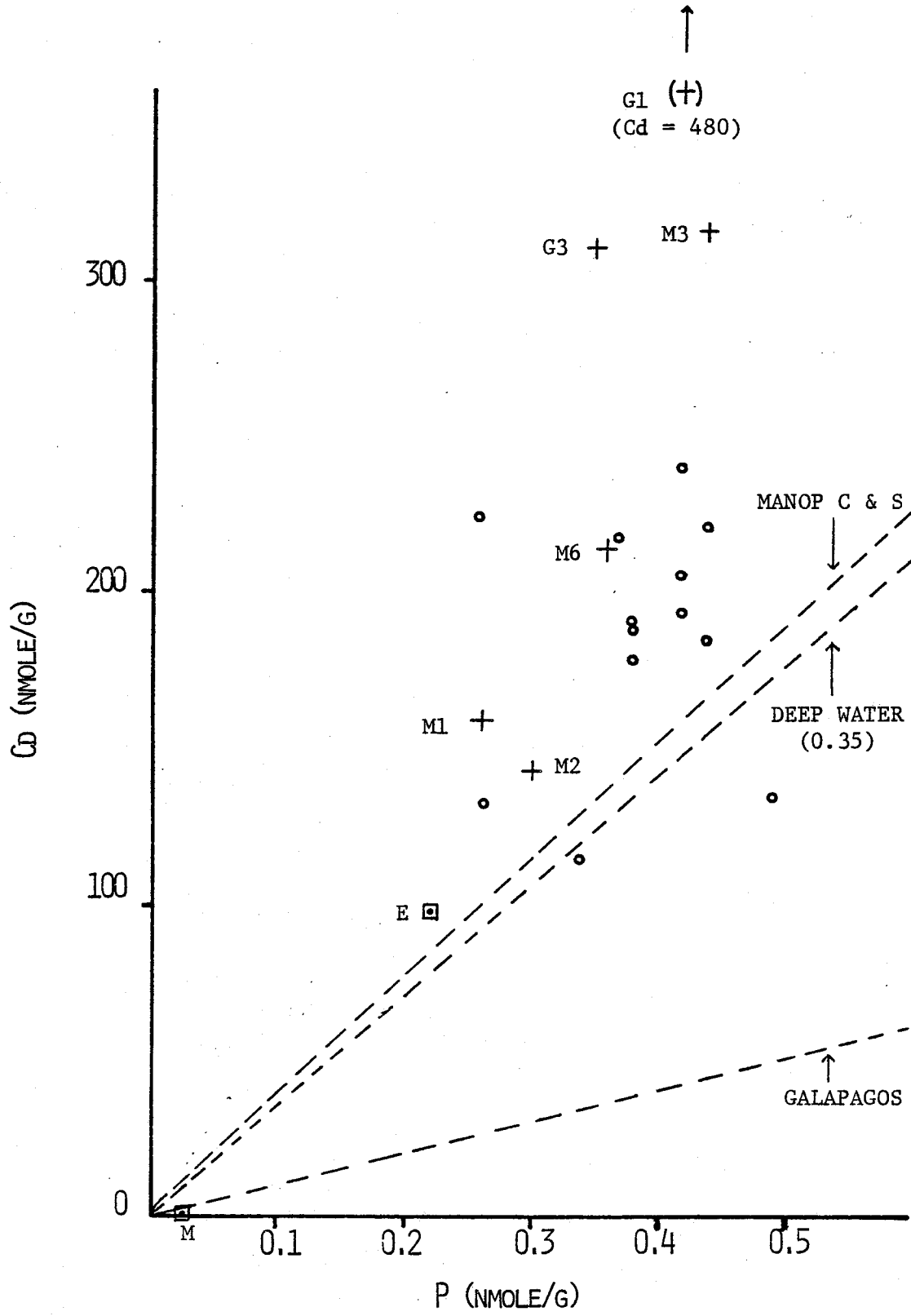
Martin et al.(1976) are plotted in Fig. IV-4. It can be seen that in nearly all cases, the ratio of Cd to P (generally  $0.4$  to  $0.7 \times 10^{-3}$ ) is well above the deep water dissolved ratio ( $0.35 \times 10^{-3}$ ). The plankton samples from MANOP sites C and S are from an oligotrophic environment which is similar to that sampled by Bruland(1980). The dissolved Cd concentrations determined at C and S (Appendix I) were higher than those of Bruland(1980), but this may be due to our lack of sensitivity, limited by a low analytical preconcentration ratio. The plankton Cd/P ratios from these sites are still higher than the water ratios. Analogous to the outflow of a continuous chemostat culture of phytoplankton, the residual concentrations of nutrients in this system are so low as to approach our current detection limits. The large analytical errors resulting are amplified through comparisons of the ratios of these small numbers.

The surface distributions are consistent with a more rapid removal of Cd than P from surface water. The deep water regeneration ratio requires that the Cd be regenerated from the plankton in the surface layer or upper thermocline before the bulk decomposition of the P carrier. This type of rapid cyclic flux of "bio-active" elements has been proposed to explain the C:N:P composition of surface organisms in open ocean environments. Based on culture results, these ratios predict a high growth rate for phytoplankton, but the apparent dissolved-nutrient concentrations would predict extreme growth limitation (Goldman et al.,1979). It is possible that Cd is tied up in a similar cycle which may be even more efficient than that of P.

Figure IV-4. Total plankton compositions: Cd vs. P.

Sample key: (•) - Bruland, et al. (1979).  
(+) - Collier, Pacific:  
    G1 - Galapagos tow 1.  
    G3 - Galapagos tow 3.  
    M1 - MANOP C tow 1.  
    M2 - MANOP C tow 2.  
    M3 - MANOP S tow 3.  
    M6 - MANOP S tow 6.  
(⊖) - Collier, Antarctic stations E and M.

(Dotted lines are dissolved ratios at each site.)



In sediment trap material from the mixed layer and upper waters of the California Current (Knauer and Martin, 1980), the average ratio of Cd/P in the total material collected was less than those measured in the Pacific plankton samples or estimated from the horizontal depletion model, applied in the same region. A continued (or enhanced) release of Cd and P within the formalin-hypersaline collection fluid further depressed the ratio in the residual particles while enriching the solution in Cd. These data support the model of a more-rapid Cd regeneration compared to that of P.

The horizontal transport model of upwelled water evolution must also be examined and refined. There are significant salinity changes in the surface waters over this Pacific transect, indicating the possibility of mixing from below with waters that could carry different Cd/PO<sub>4</sub> ratios. The particulate ratio cannot be extracted from this system without the compositions and mixing ratios of all the various end-members involved.

From a geochemical point of view, it is useful that many of the element-carrier ratios are roughly constant in the plankton samples. This ratio allows the direct prediction of the biogenic flux of each trace element in terms of the organic cycles. The flux can then be compared to the dissolved distributions of those trace elements. The fluxes will be estimated using the major components of biogenic particulate material and is independent of other components of the trace element cycles (such as hydrothermal or authigenic components).

