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THE TRACE ELEMENT GEOCHEMISTRY OF  
MARINE BIOGENIC PARTICULATE MATTER

by

ROBERT WILLIAM COLLIER

S.B., Massachusetts Institute of Technology, Cambridge  
(1974)

M.S., California Institute of Technology, Pasadena  
(1975)

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Signature of Author ..  
Joint Program in Oceanography, Massachusetts Institute  
of Technology - Woods Hole Oceanographic Institution,  
and Department of Earth and Planetary Sciences,  
Massachusetts Institute of Technology, November, 1980

Certified by ..  
Thesis supervisor

Accepted by .....  
Chairman, Joint Oceanography Committee in the Earth  
Sciences, Massachusetts Institute of Technology -  
Woods Hole Oceanographic Institution

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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

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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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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.

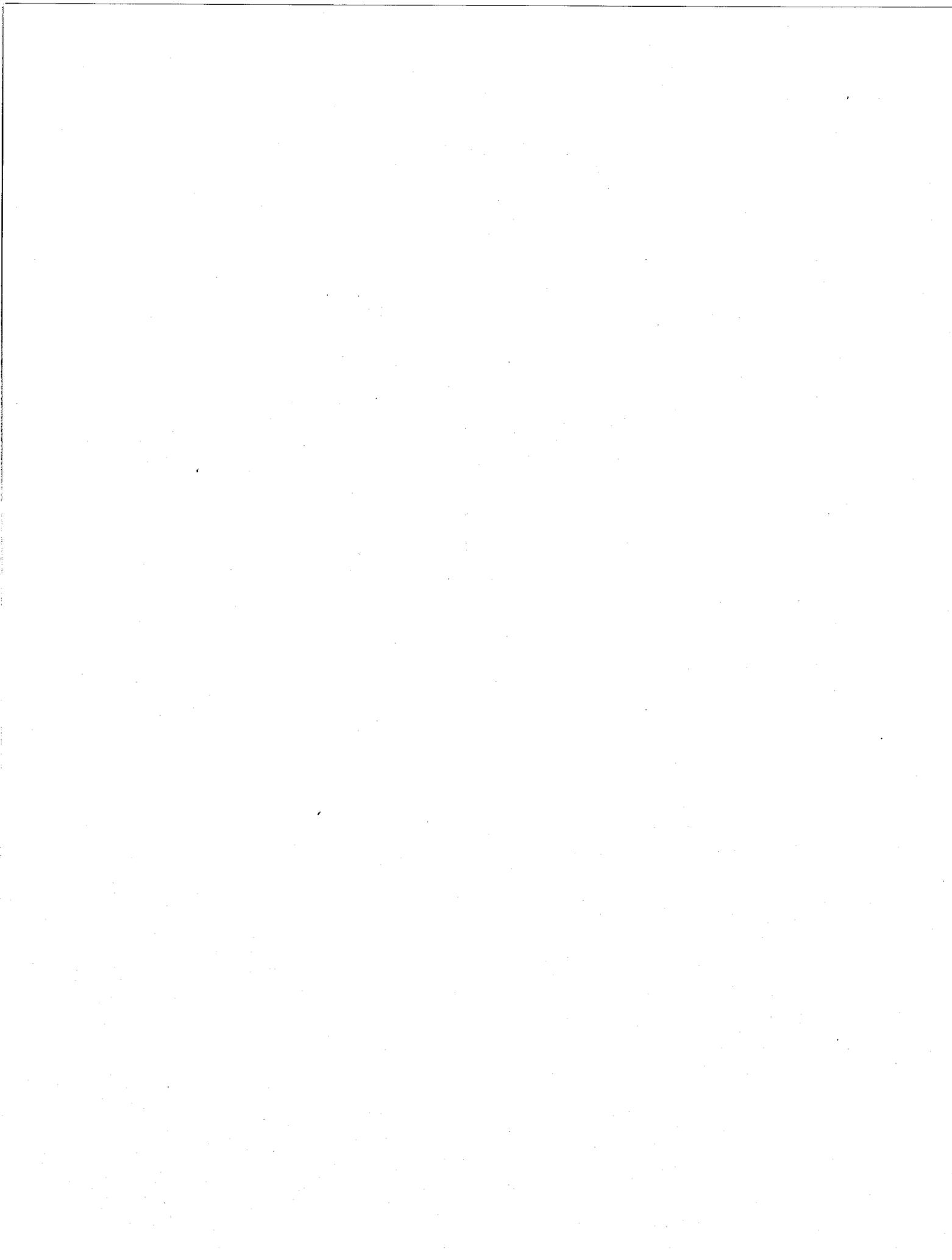


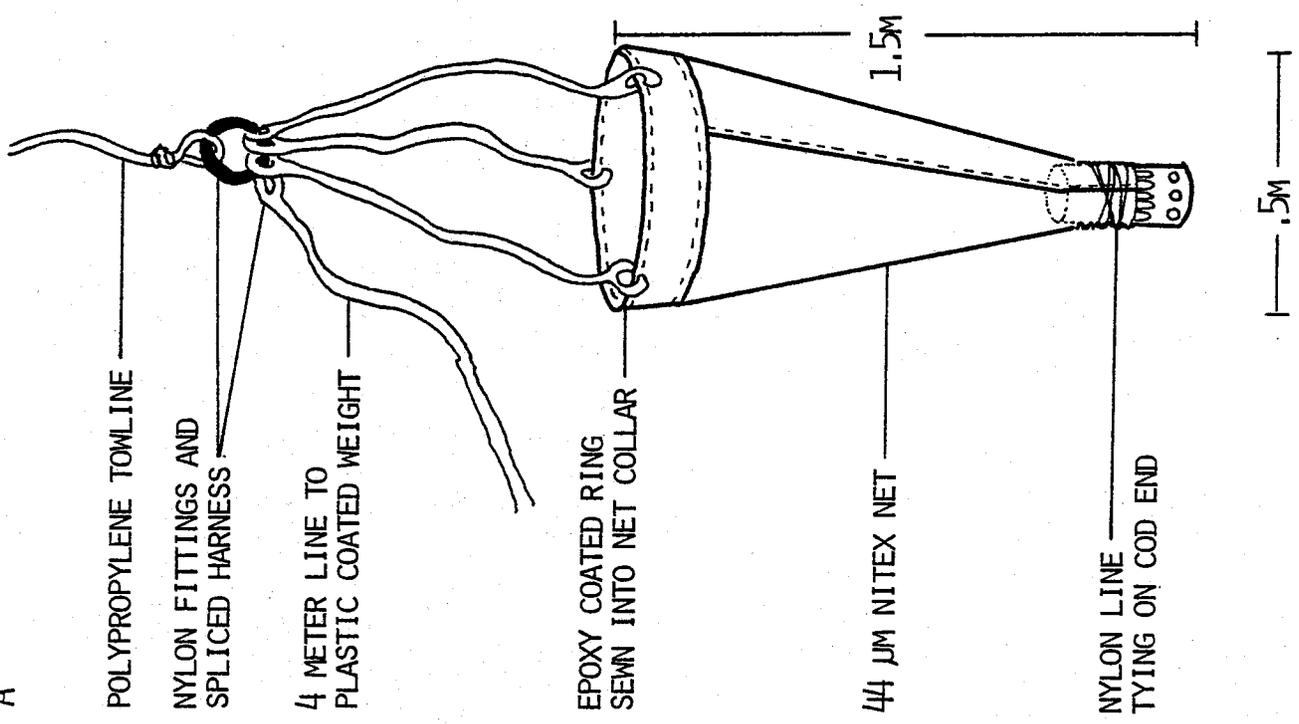
Figure II-1. Plankton sampling equipment.

A) Net.

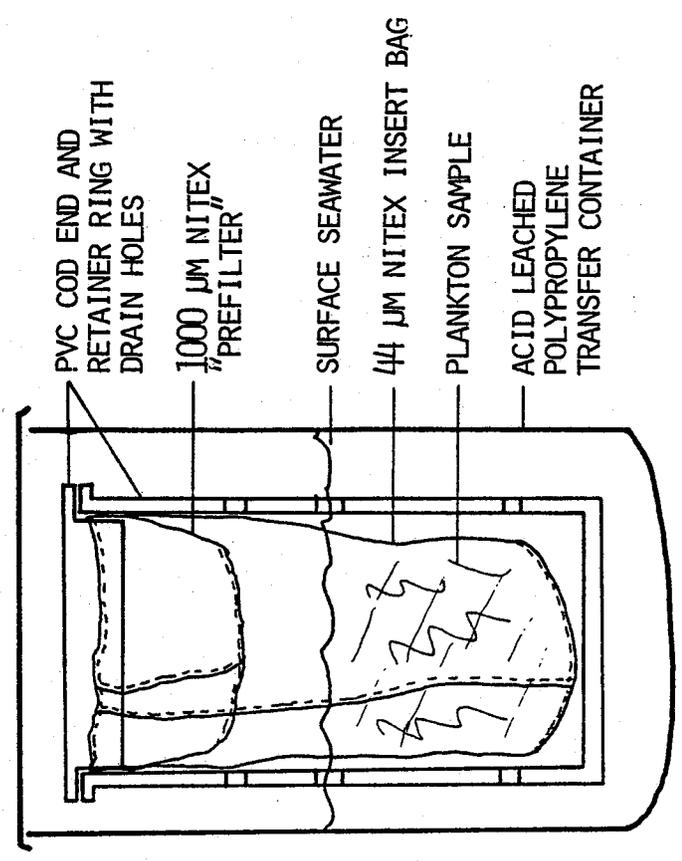
B) Cod end.



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.

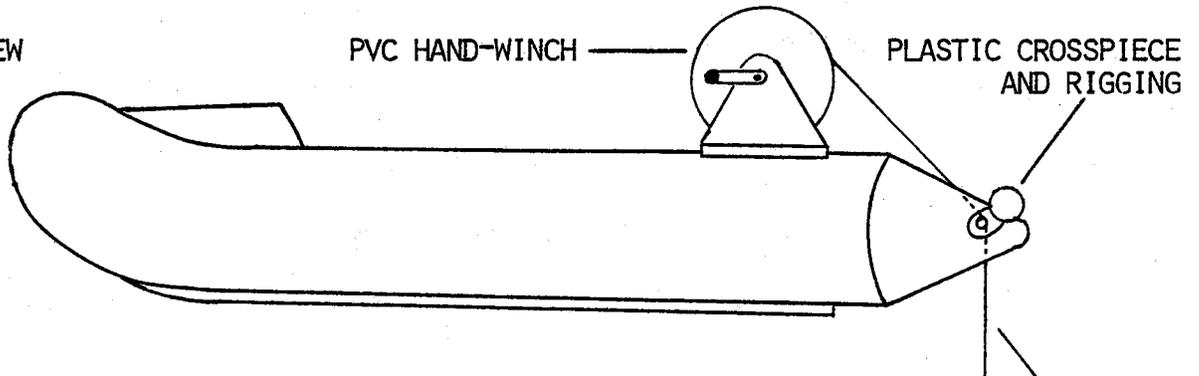
The hand-towing method, although far superior to normal ship tows in preventing contamination, was severely limited by wind, sea-state, and the low concentration of plankton found in the surface waters of oligotrophic environments. Therefore some plankton tows were collected from the main research vessel. 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.

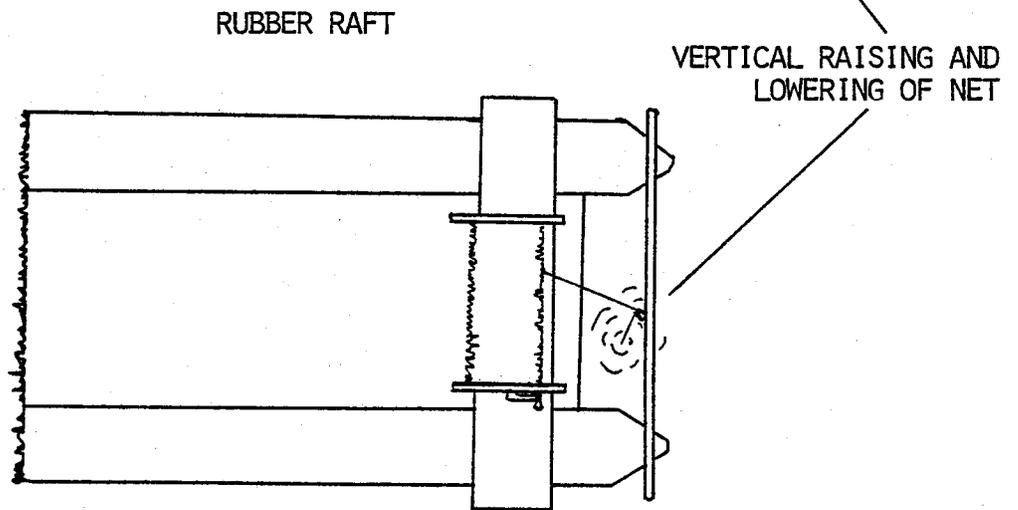
A) Zodiac rigging.

B) Ship and boom rigging.

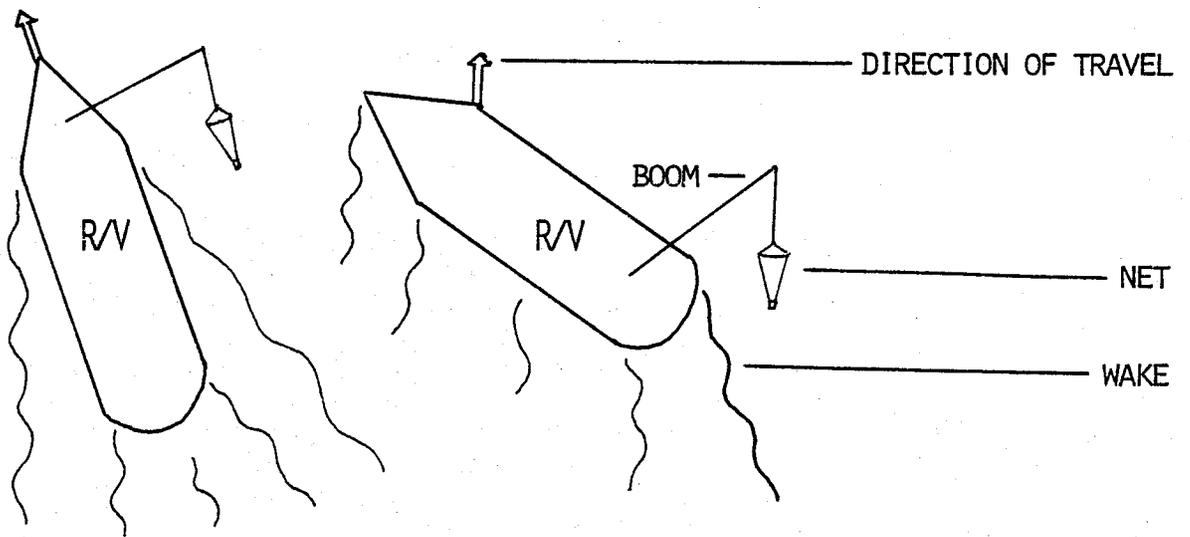
SIDE VIEW



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.

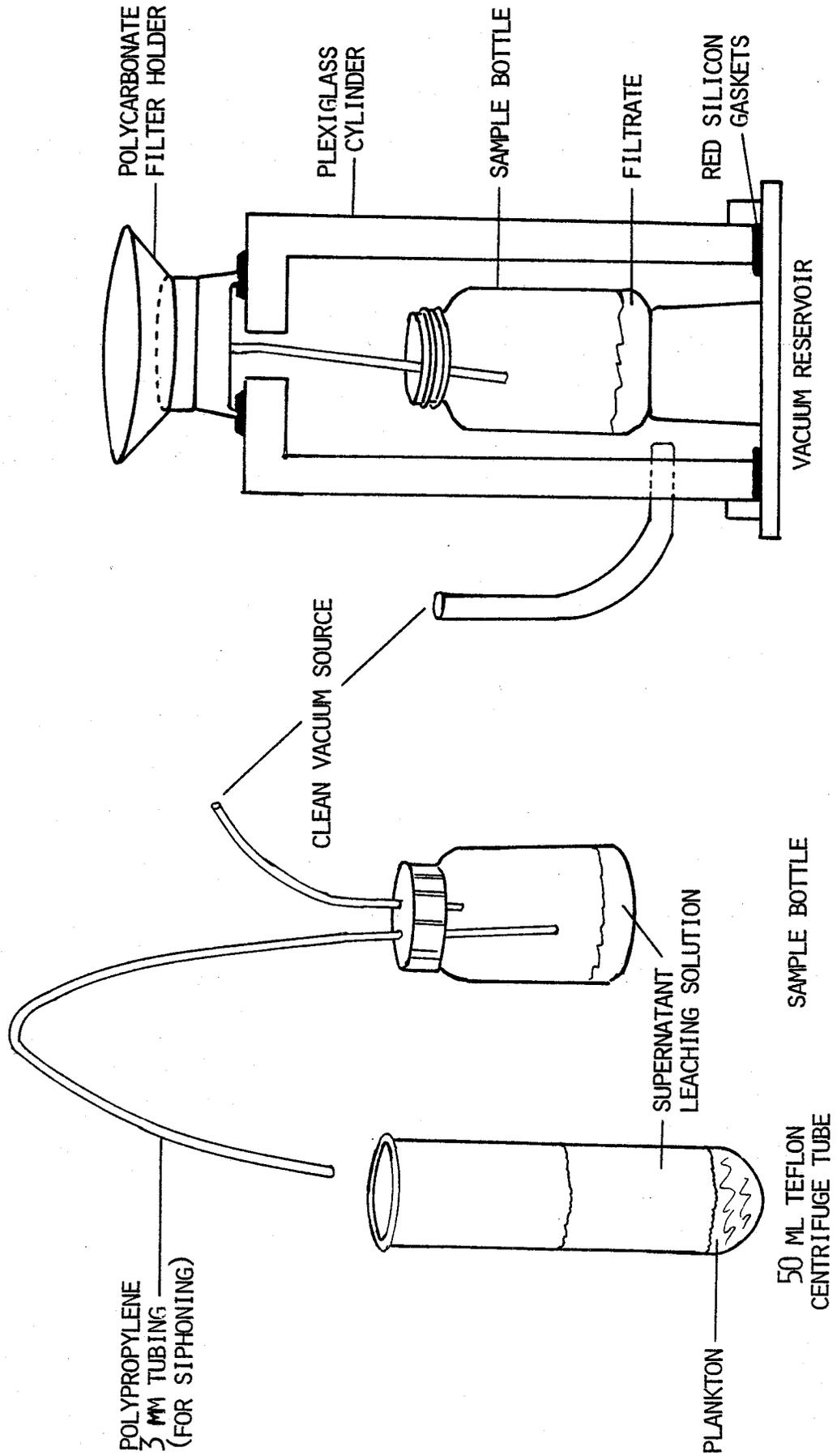


Table II-1. CHEMICAL REAGENTS USED IN LEACHING AND ANALYSIS

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.)

---

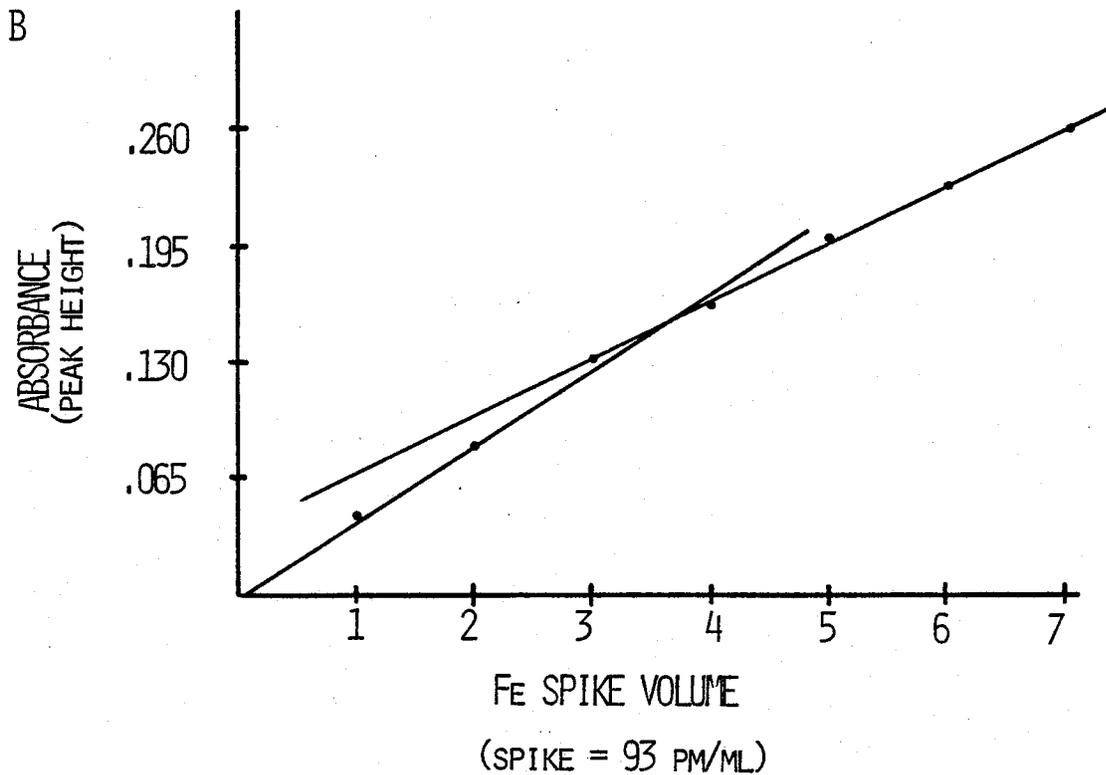
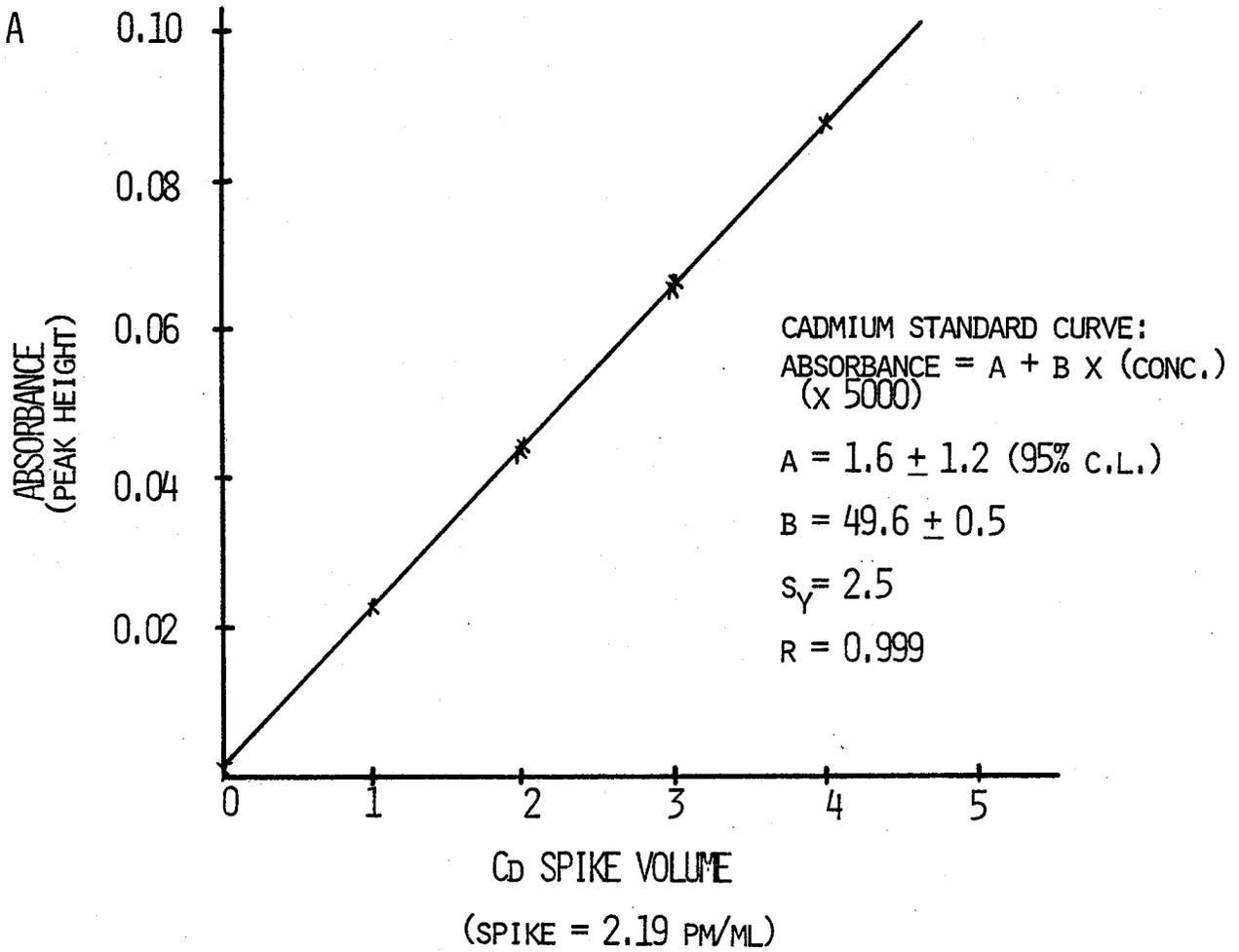
Analysis 1 - dilution X17.5  
slope  $5 \times 10^{-3}$  abs units/pm

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

---

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.

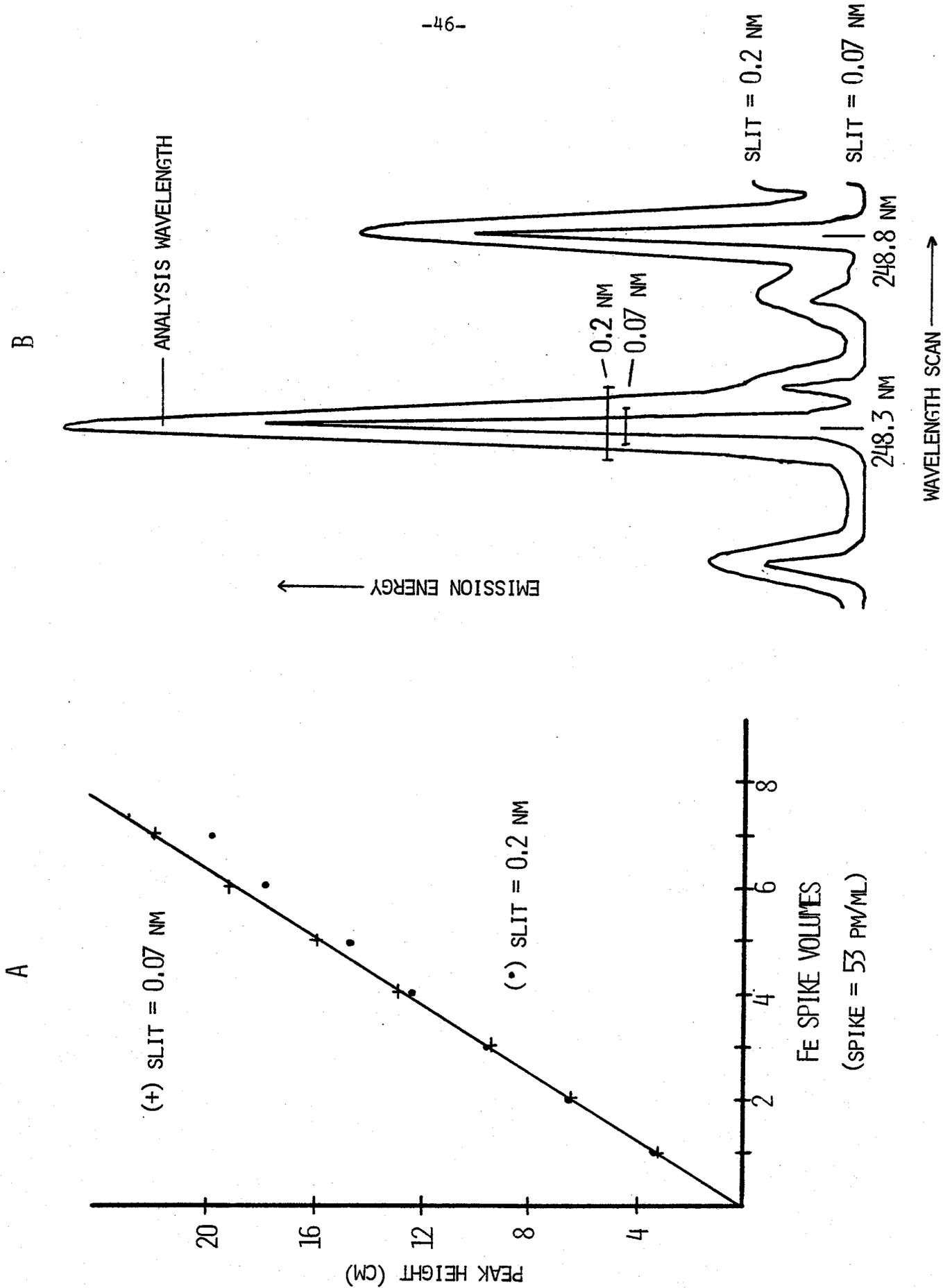
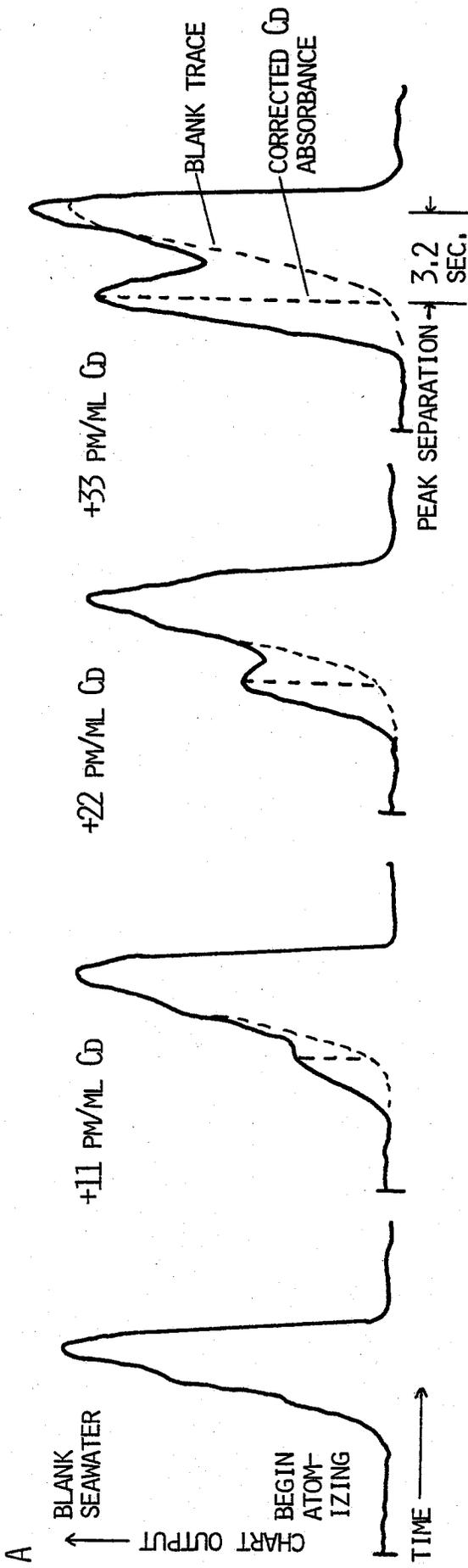
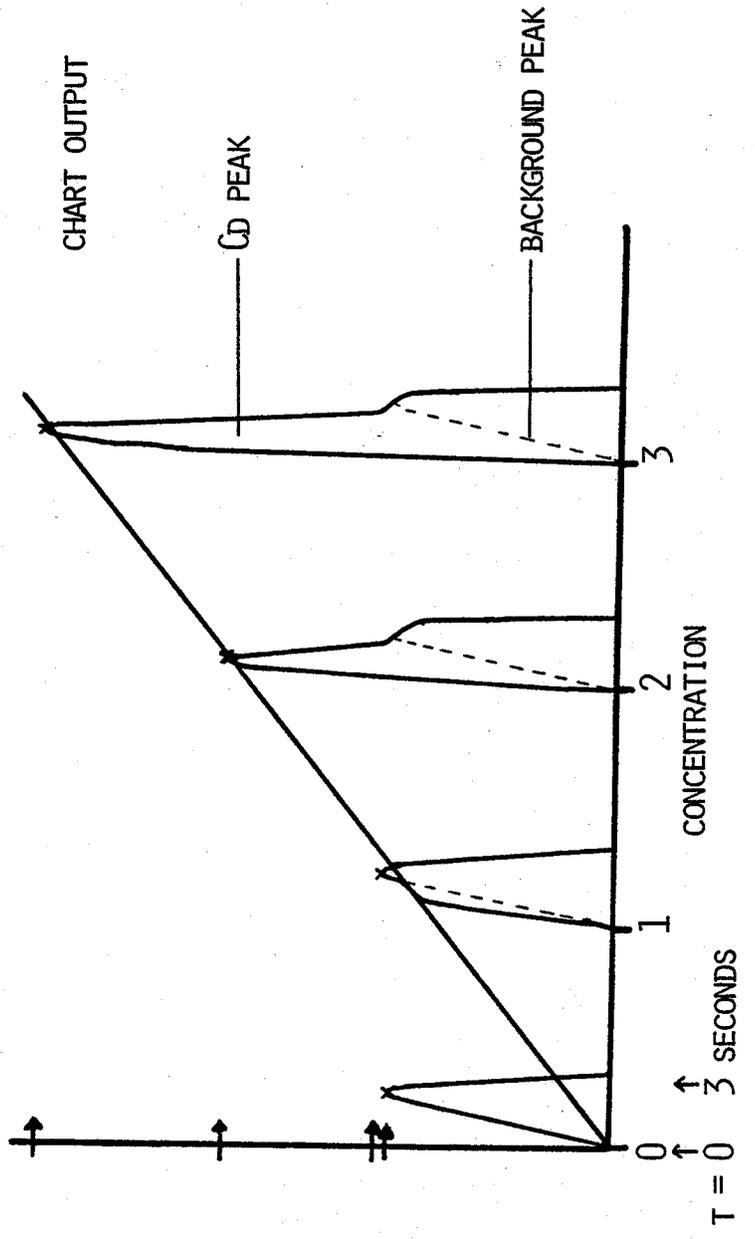


Figure II-6. Background absorbances in Cd determinations.

- 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	
Ni	11.7 1.4	13.5 1.6	35.1 5.4	27.4 3.7	21.1 2.4	21.6 2.5	
Cd	26.3 3.2	37.2 5.1	55 4.5		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 1.4	
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  
 Seawater 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	14.9
Si								
Cu	14.8 3.6	14.6 3.6	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	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	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	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	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	2	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

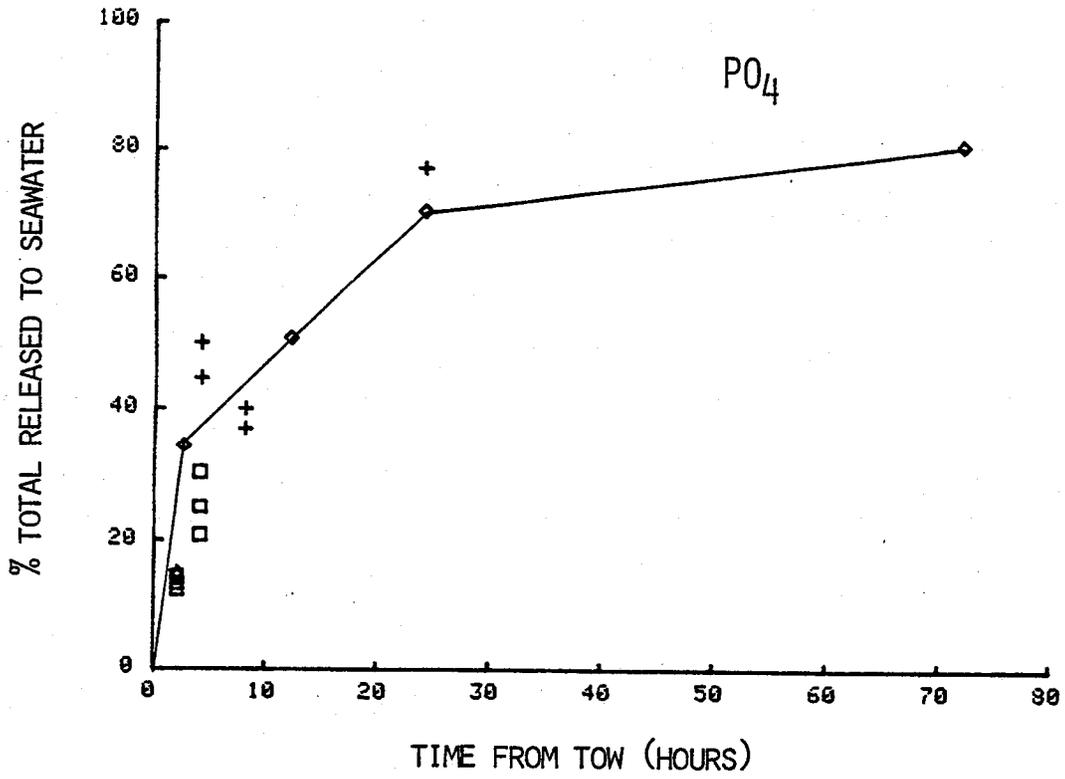
Figure III-1. Seawater release:  $PO_4$  and Cd vs. time.

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

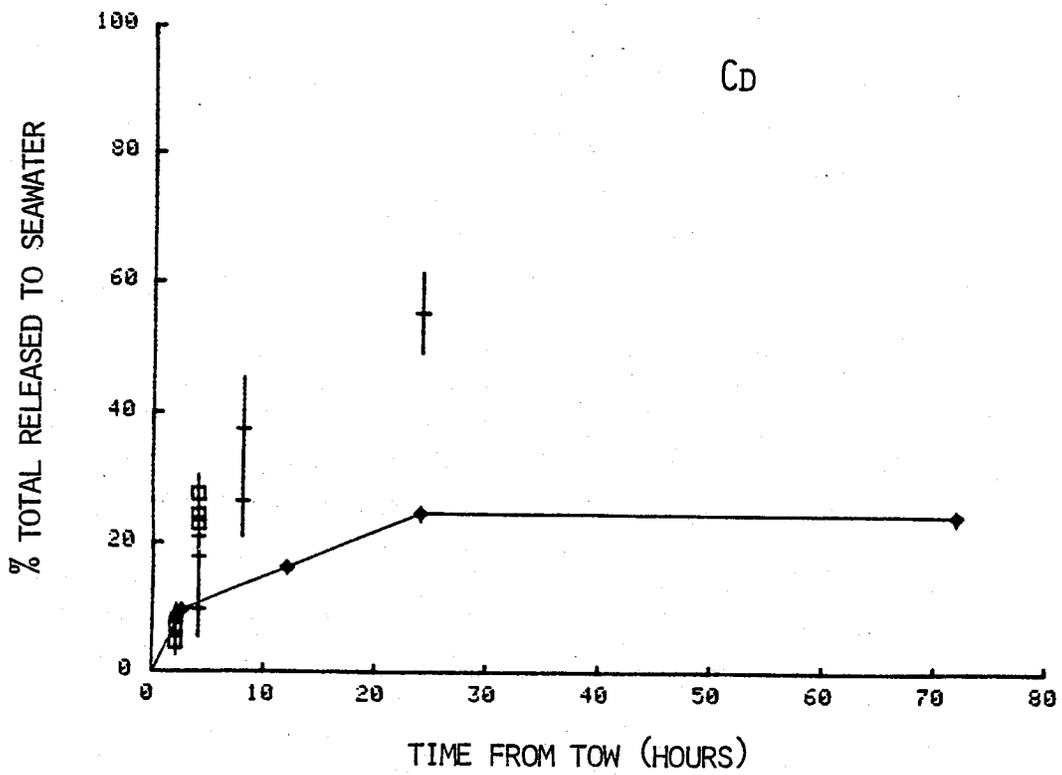


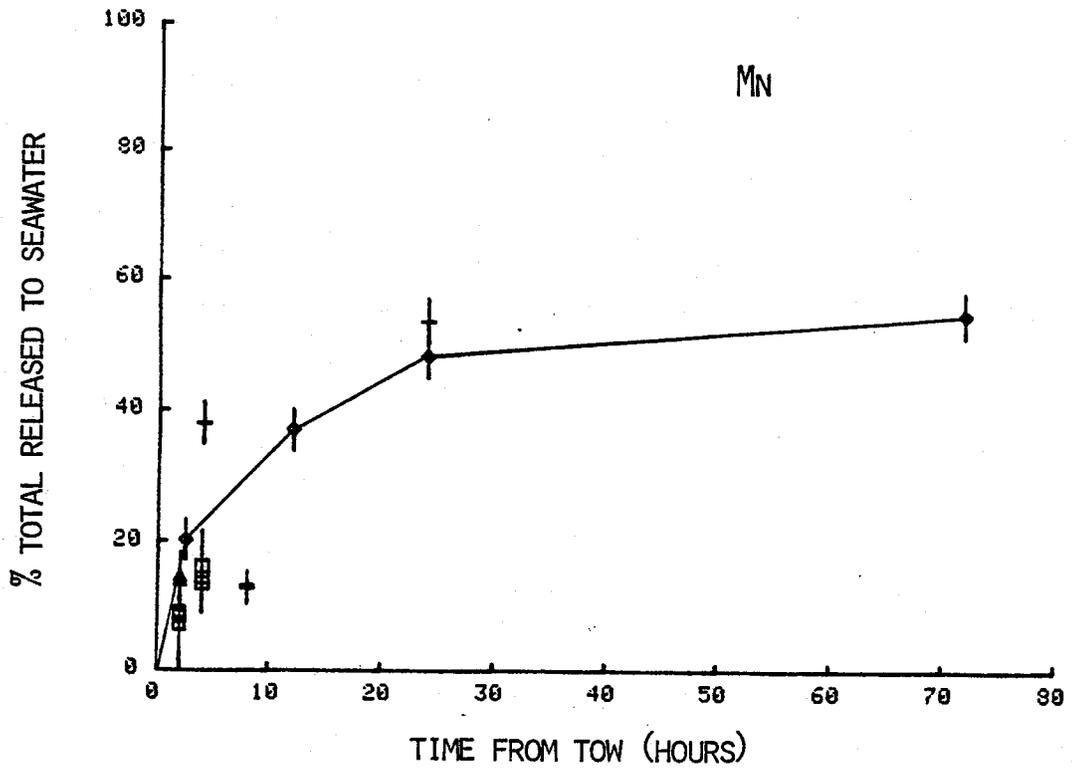
Figure III-2. Seawater release: Mn and Ni vs. time.

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

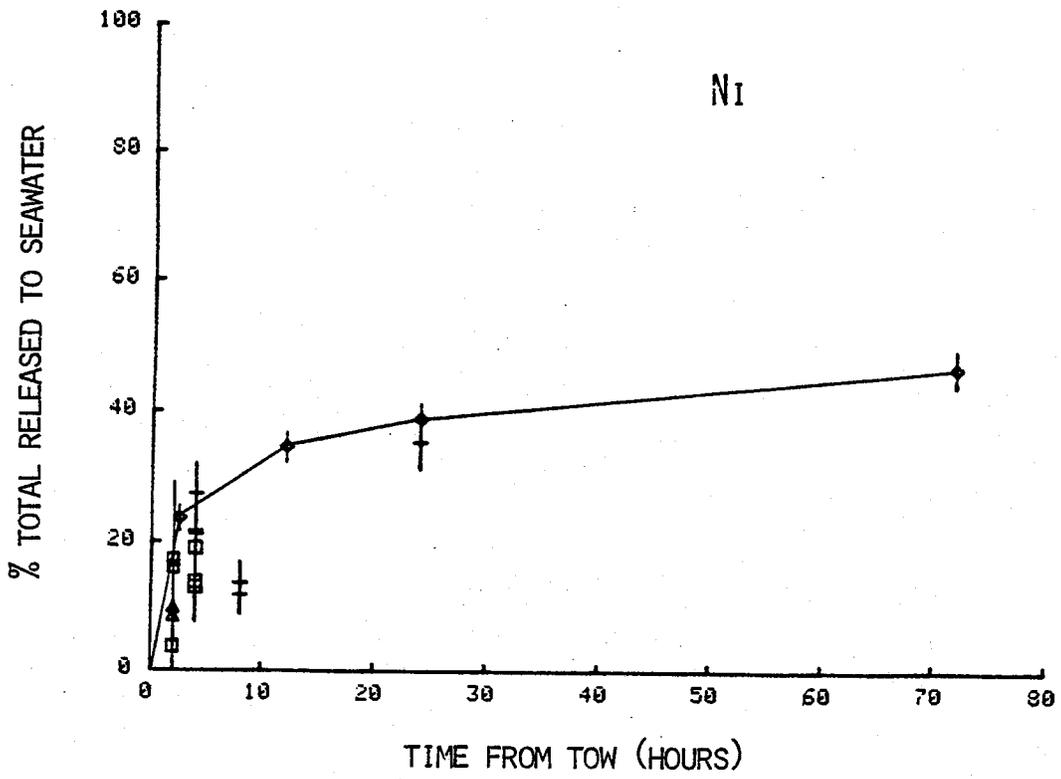


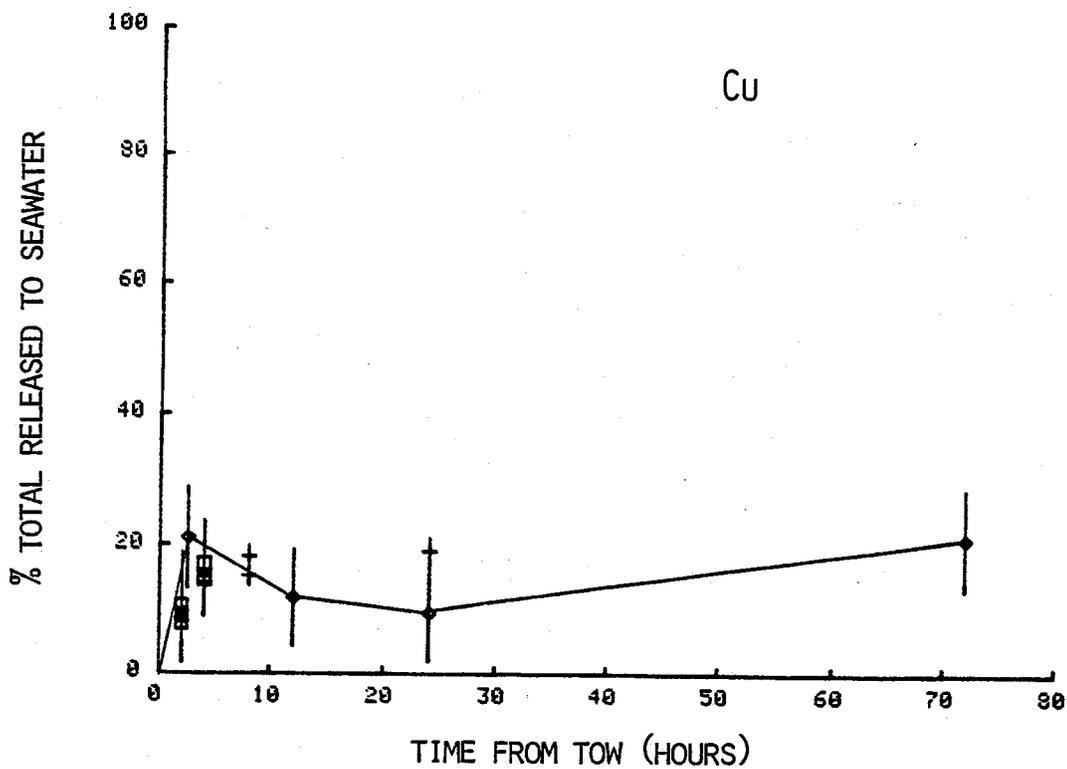
Figure III-3. Seawater release: Cu and Fe vs. time.

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

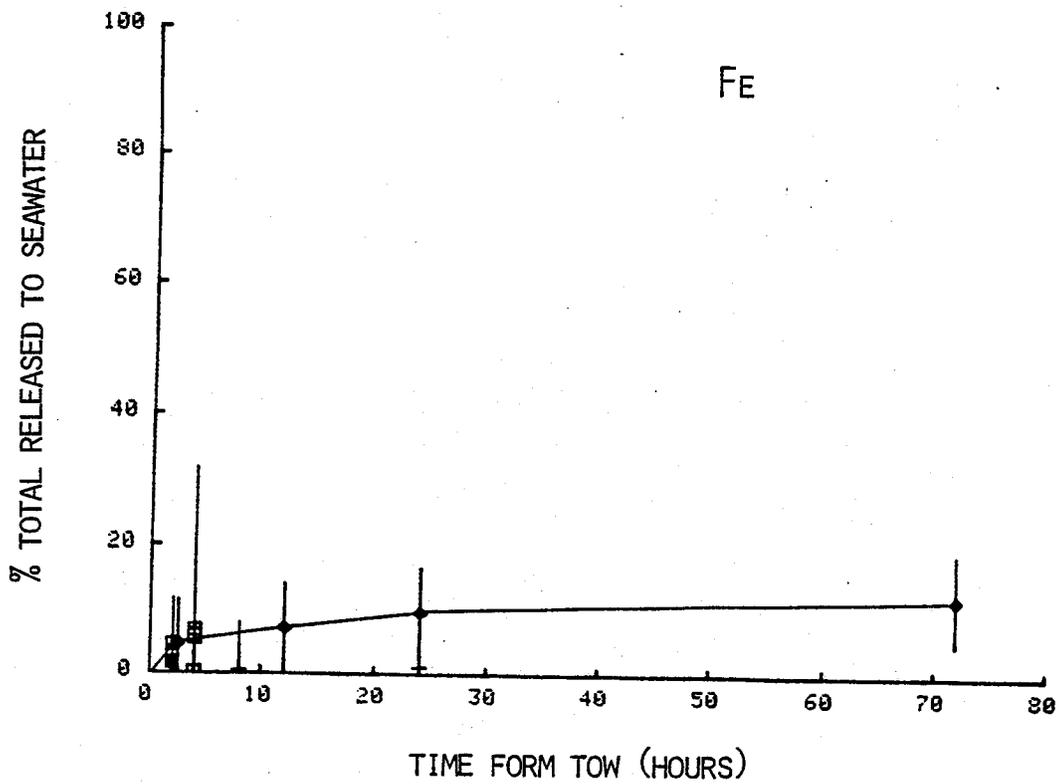


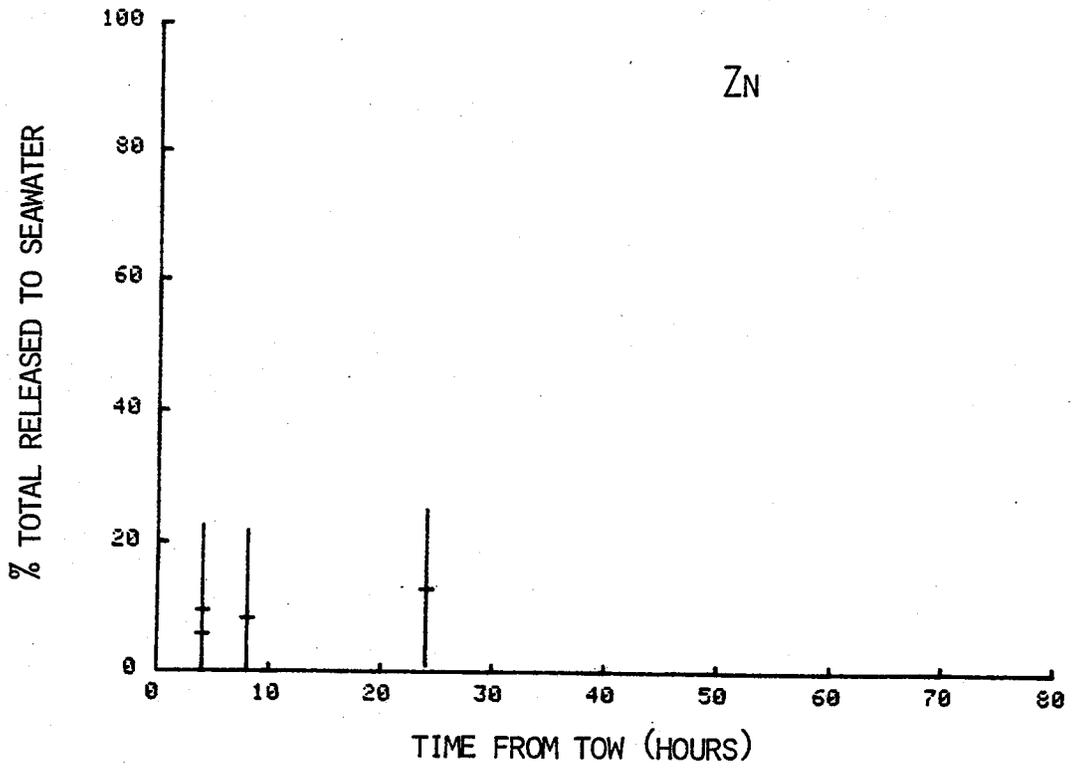
Figure III-4. Seawater release: Zn and Al vs. time.

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

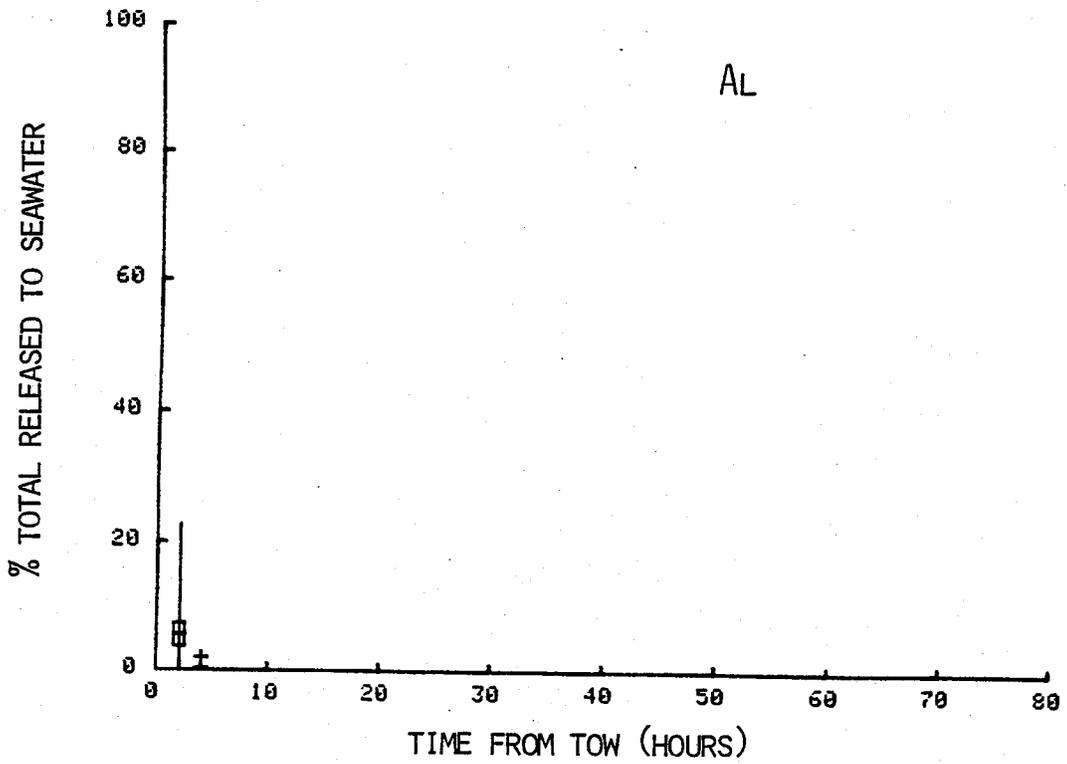


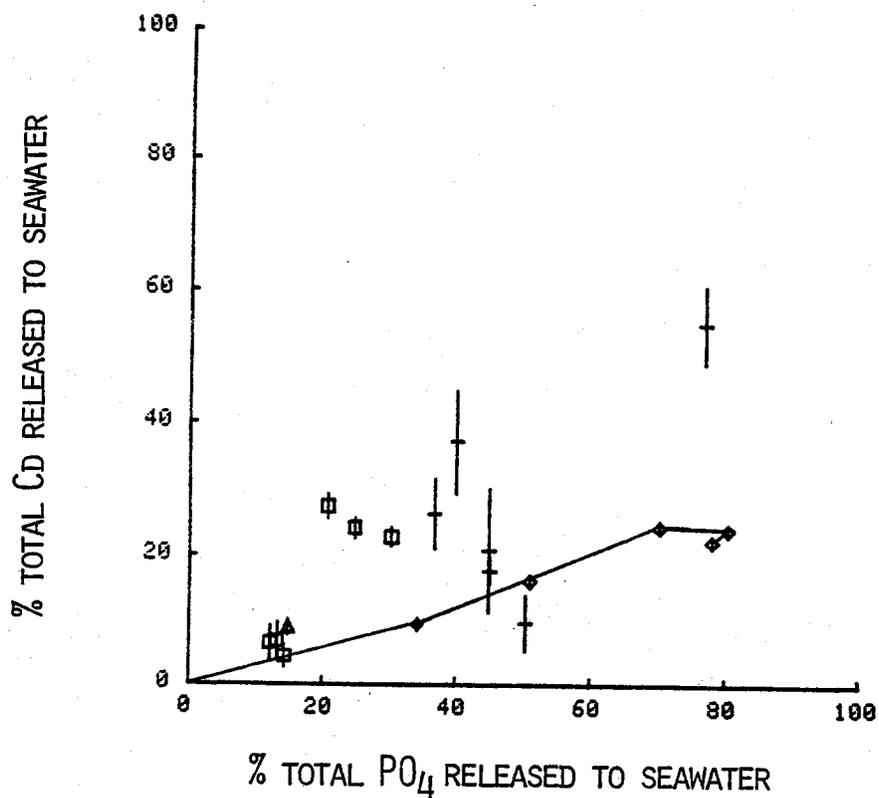
Figure III-5. Seawater release: Cd and Mn vs. P.

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

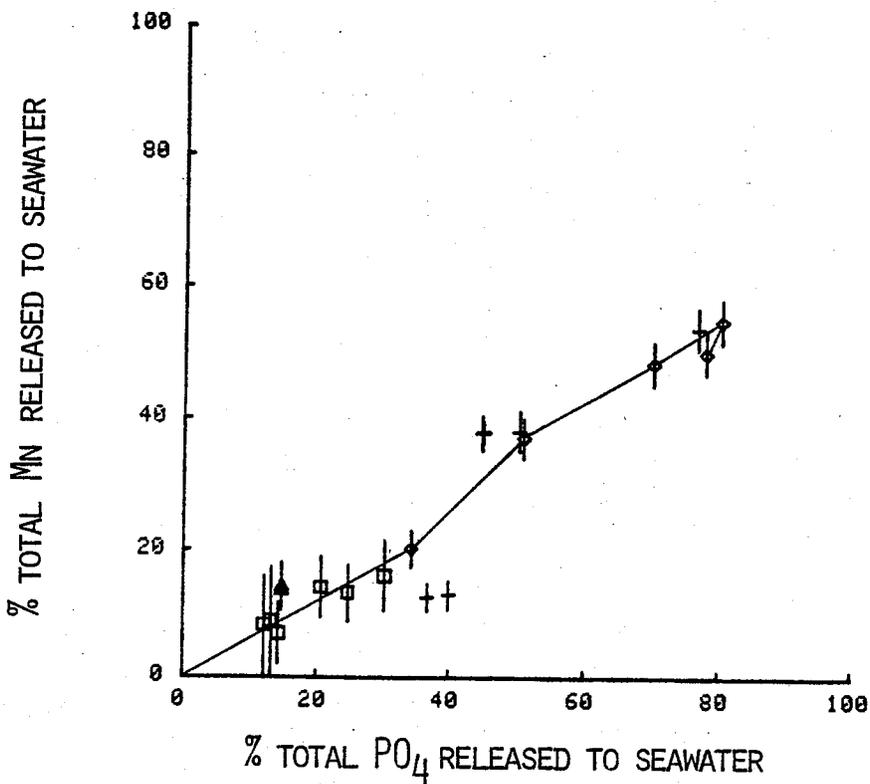


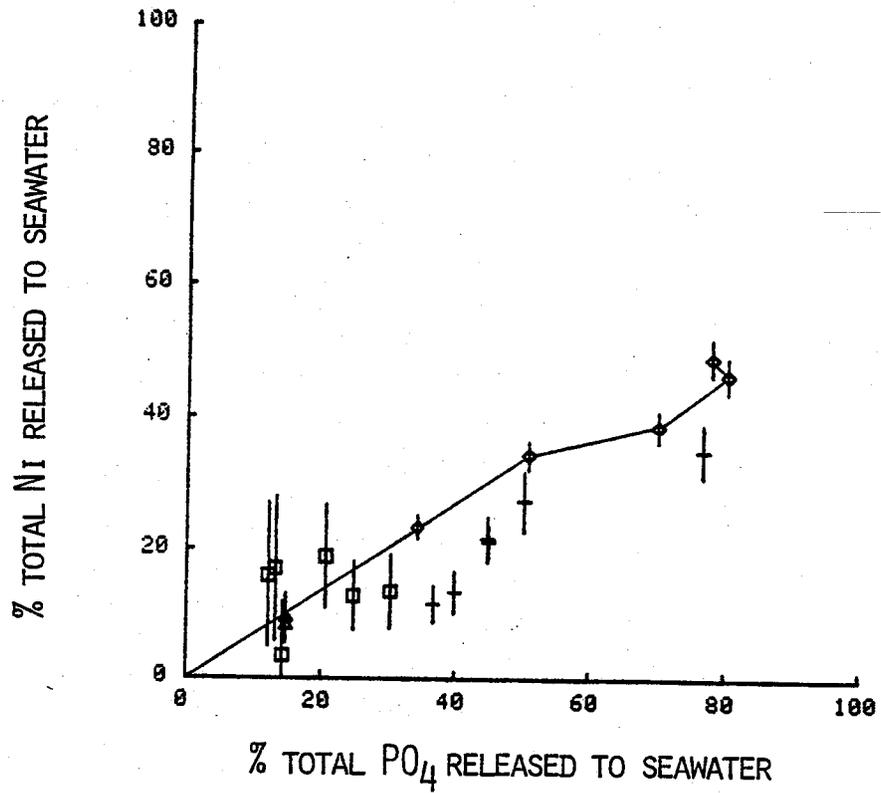
Figure III-6. Seawater release:  $PO_4$  and Mn vs. Ni.

SYMBOL KEY  
(for figures 1 - 6)

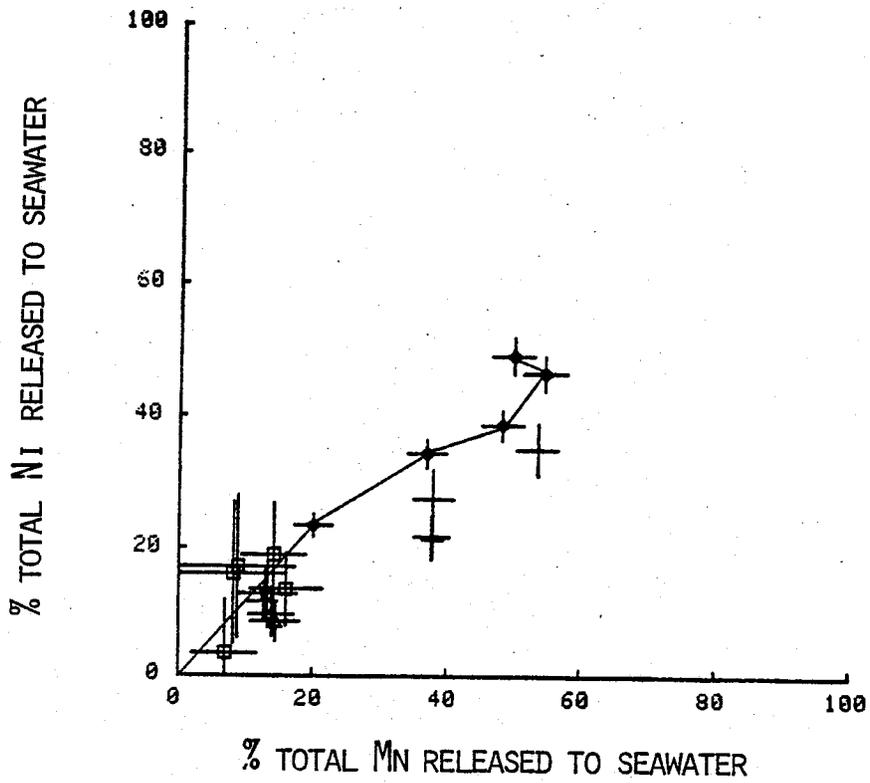
- + Galapagos Tow 1 & 3
- MANOP C Tow 1 & 2
- △ MANOP S Tow 3
- ◇ MANOP S Tow 6 (points connected)

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 (cumulative sw + dw)	.38 (.38)	.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

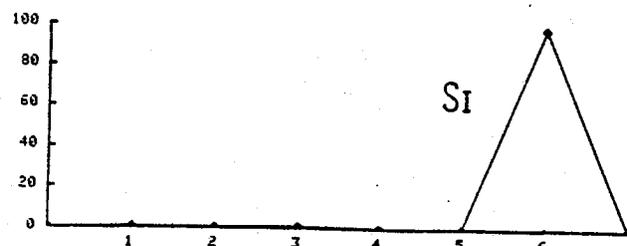
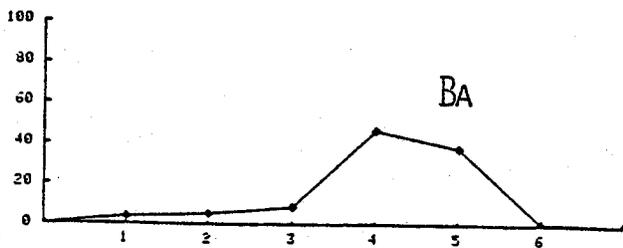
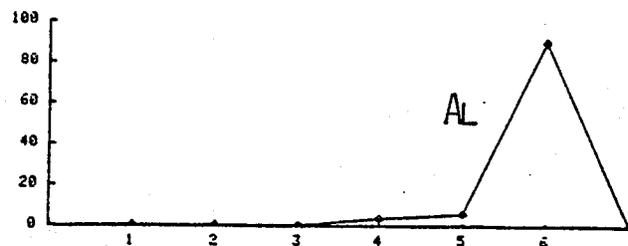
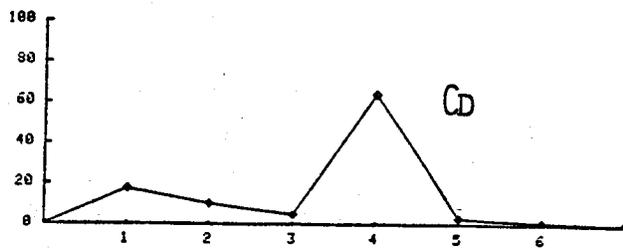
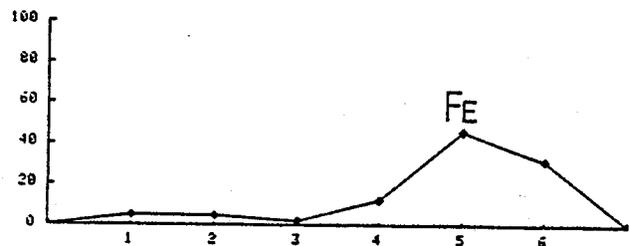
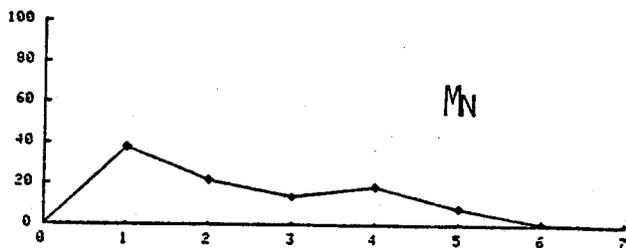
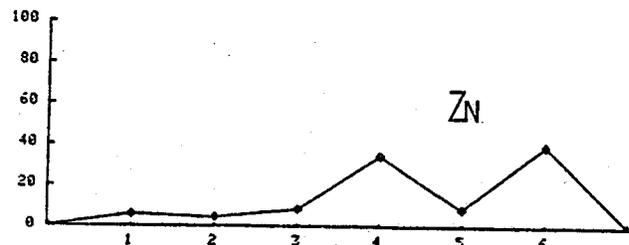
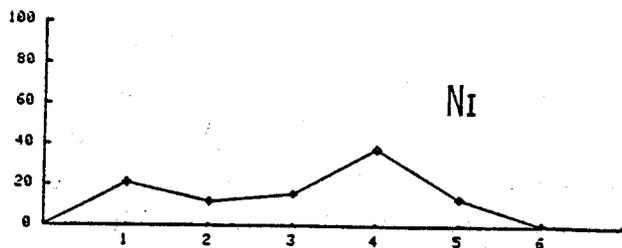
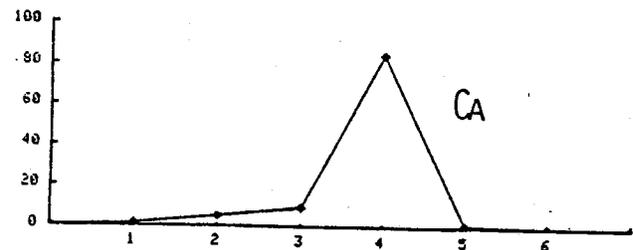
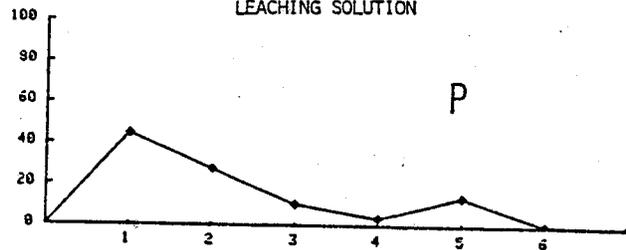
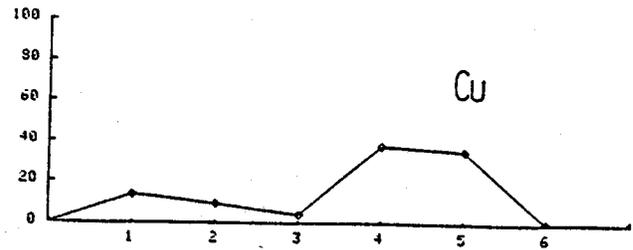
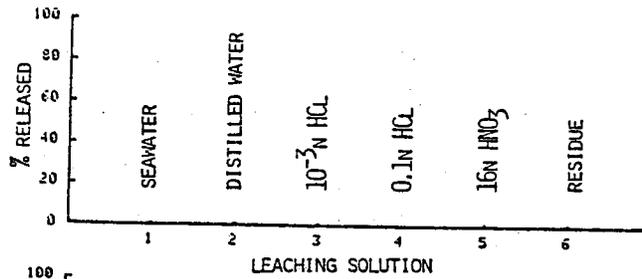


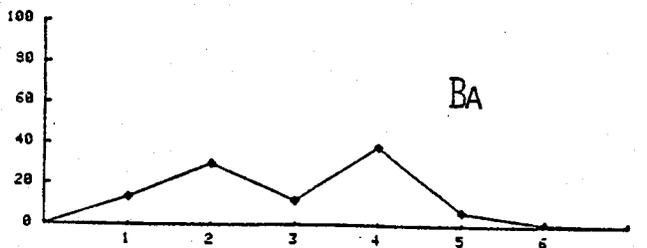
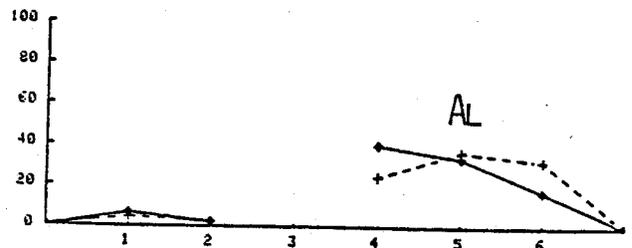
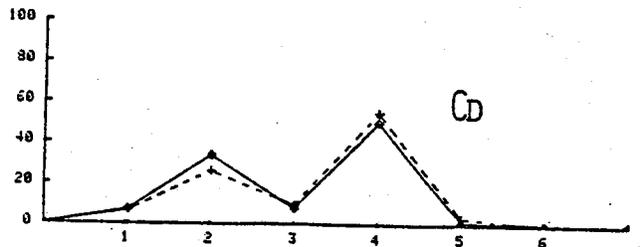
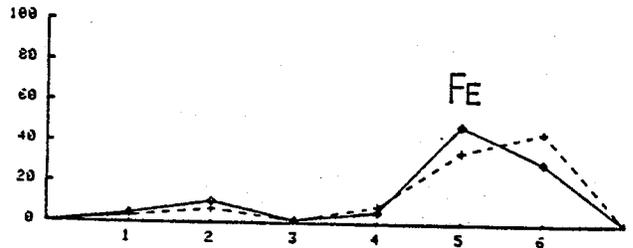
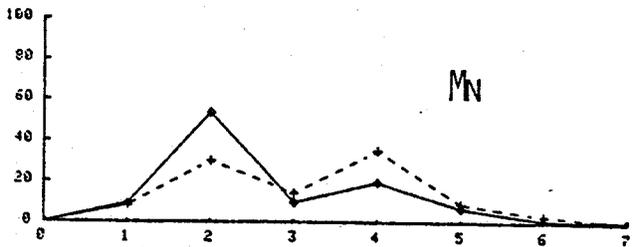
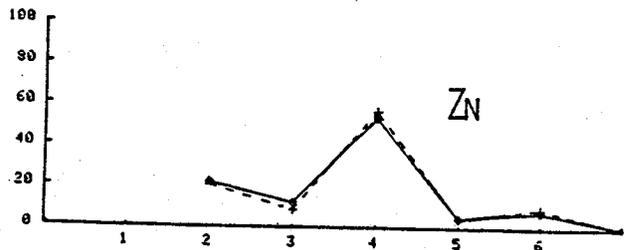
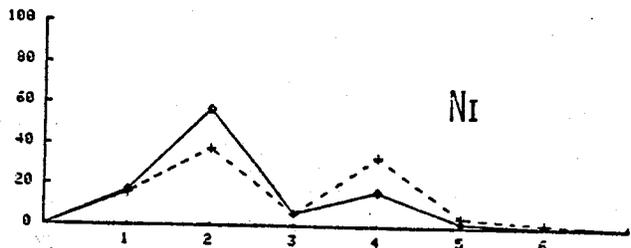
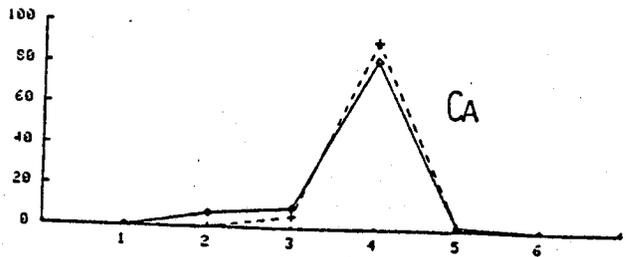
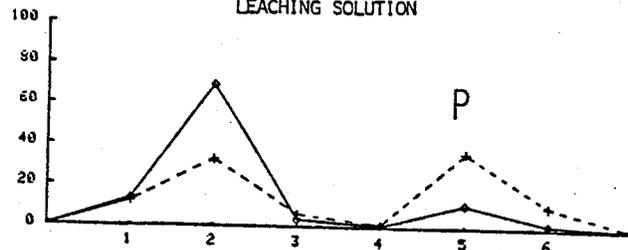
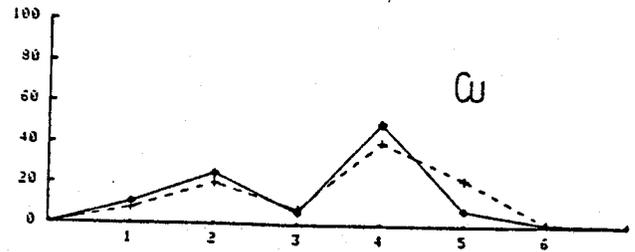
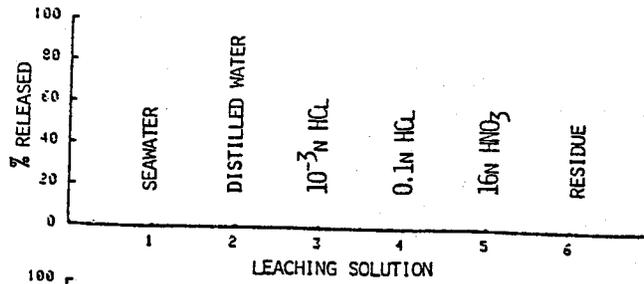
Figure III-8. Acid leaching series; MANOP C, tow 2.

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 1977	9 7.8	.54 .36	40% 60%		1.7 1.2	70% 100%	2.2 1.7	1% 2%	1.7 2.2	5% 4%	13 27	0.6% 0.3%							
MANOP C Tow 1 plankton Tow 2	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.

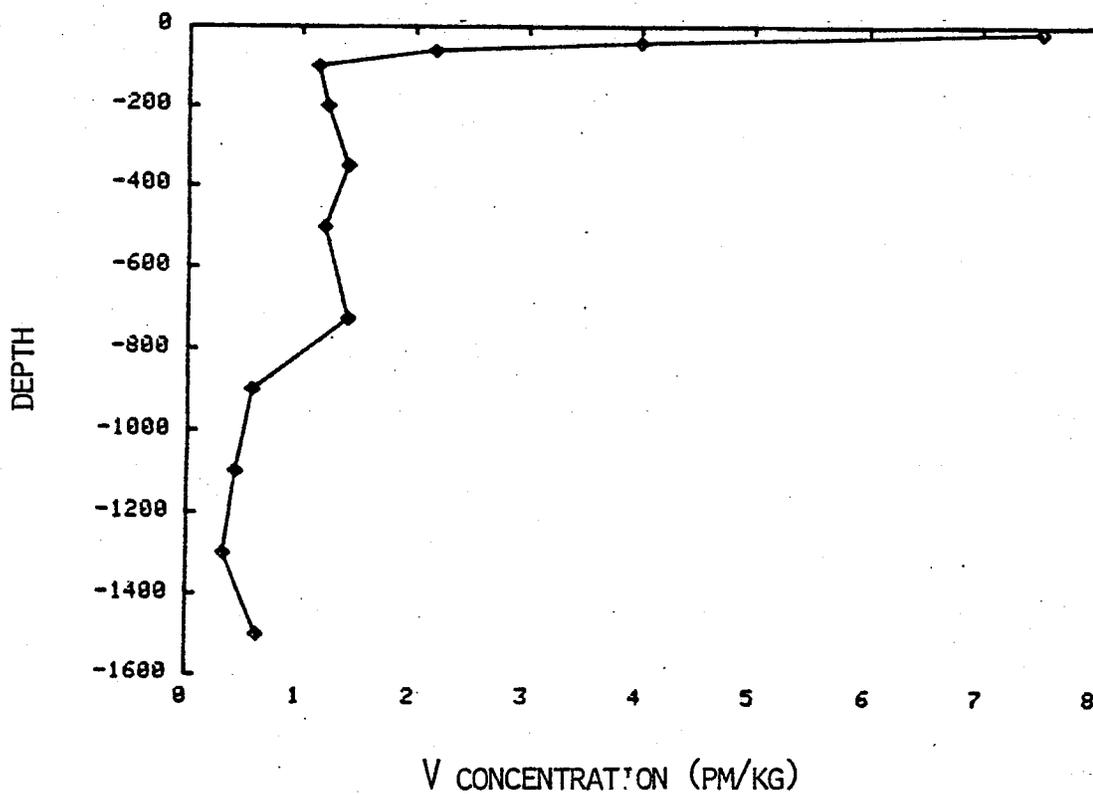
The comparison made here between the North Atlantic and the Pacific particulate matter shows the importance of considering both terrigenous and biogenic material in the geochemical cycle of an

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

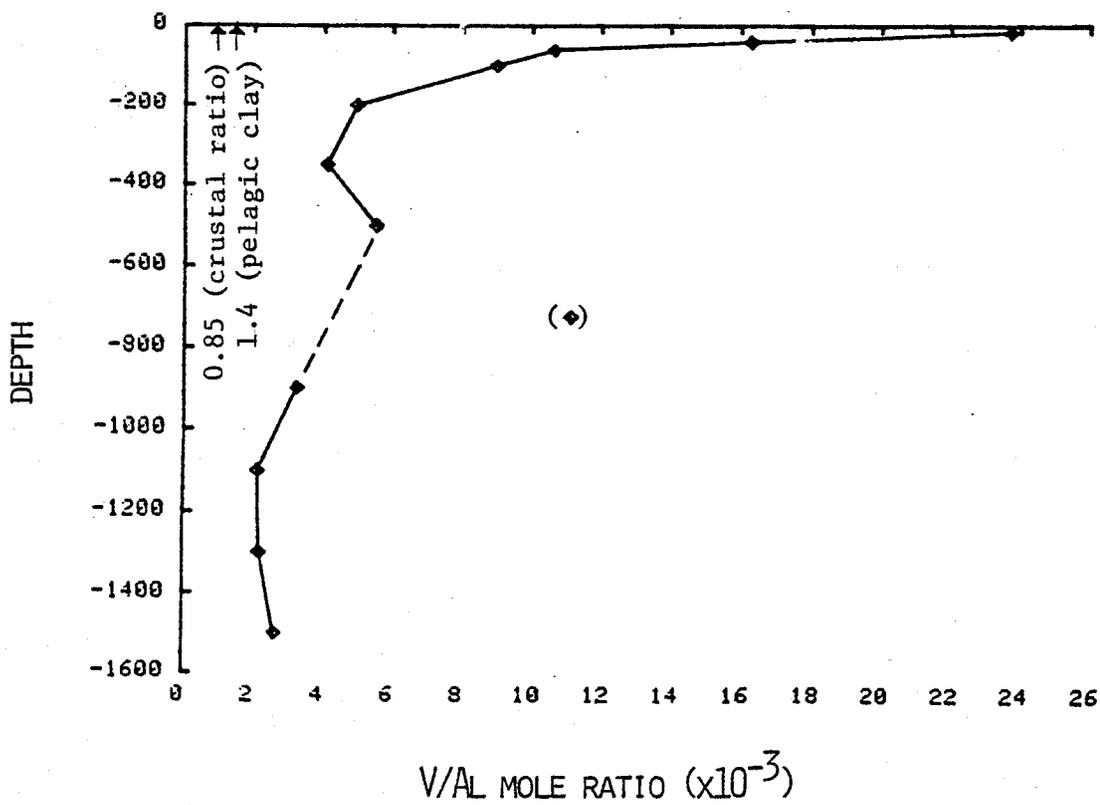
A) Particulate V vs. depth.

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	HNO <sub>3</sub>	Residual
Galapagos Tow 3	7.8 µm/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 µm/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	Zn*	.35	2.4	3.0	Plankton Ratios to P	5	3	3.3
		-	-	-			-	-
(x10 <sup>-3</sup> )	Cu	2.6	17	28	(x10 <sup>-3</sup> )	.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	
	Cd	9	1.5	1.8	Relative Seawater Release Ratio	1.6	1.6	3.0
Ratio of Plankton to Water Ratios	Zn	14	1.3	1.1		6		
		-	-	-		-	-	-
(α)	Cu	.22	.03	.02	(β)		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

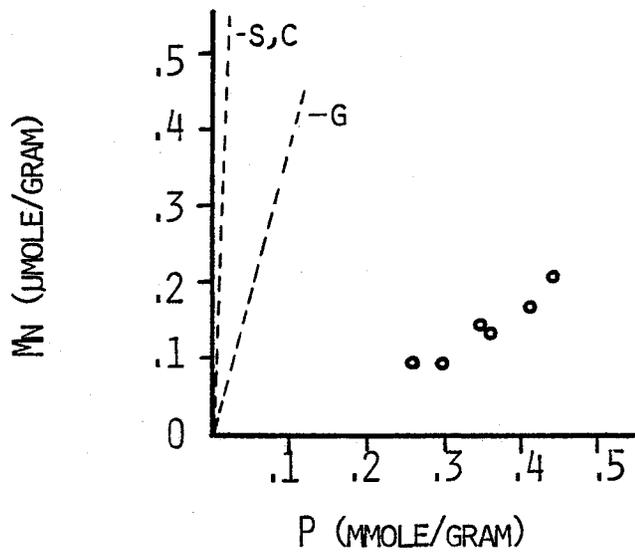
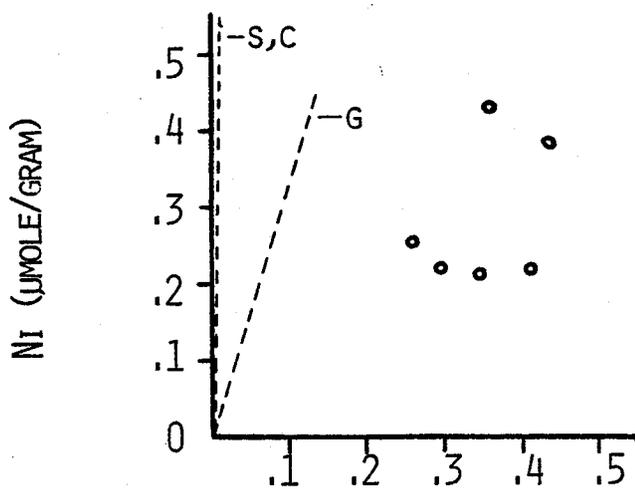
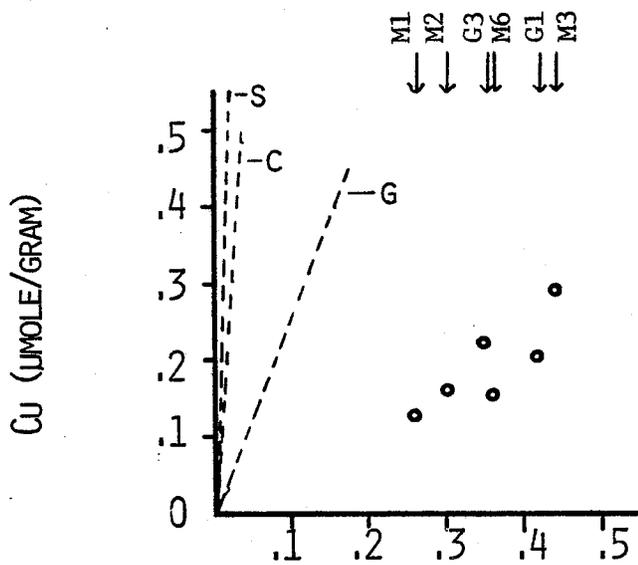
Table IV-4 Surface water depletion vs. plankton ratios. ( $\times 10^{-3}$ )

	$\Delta \text{Cu} / \Delta \text{P}$	$\Delta \text{Ni} / \Delta \text{P}$
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).

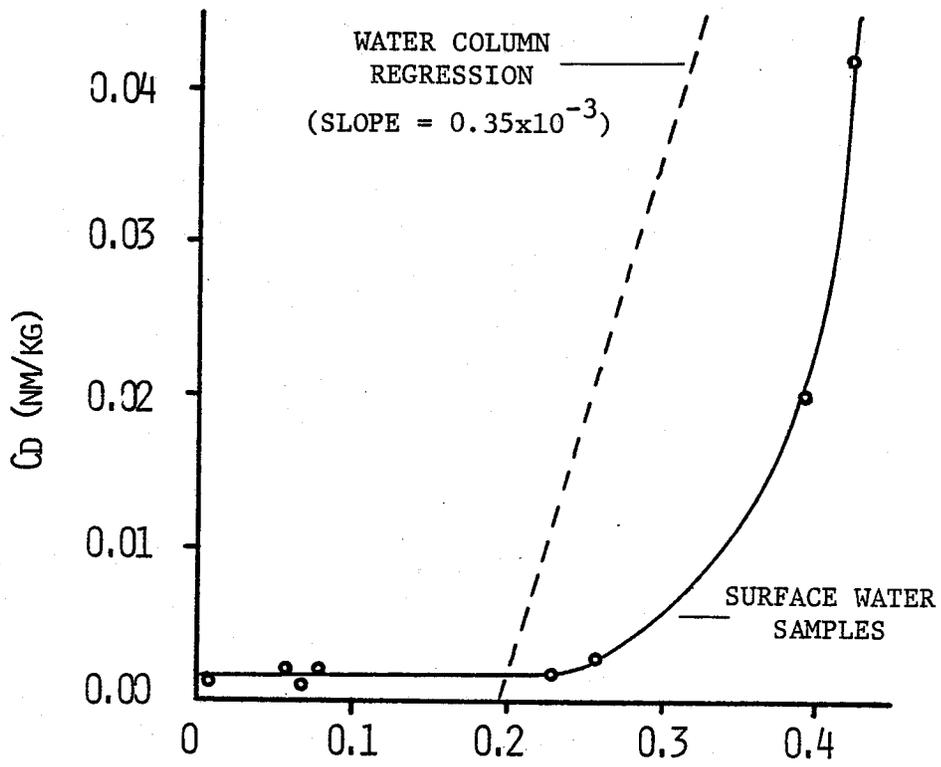
After the dissolved Cd concentration has been depressed to near the detection limit, the concentration of  $\text{PO}_4$  continues to decrease - implying a flux of relatively Cd-poor particles out of the nutrient-depleted waters. This distribution (Fig. IV-3), coupled with the model describing particulate 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.

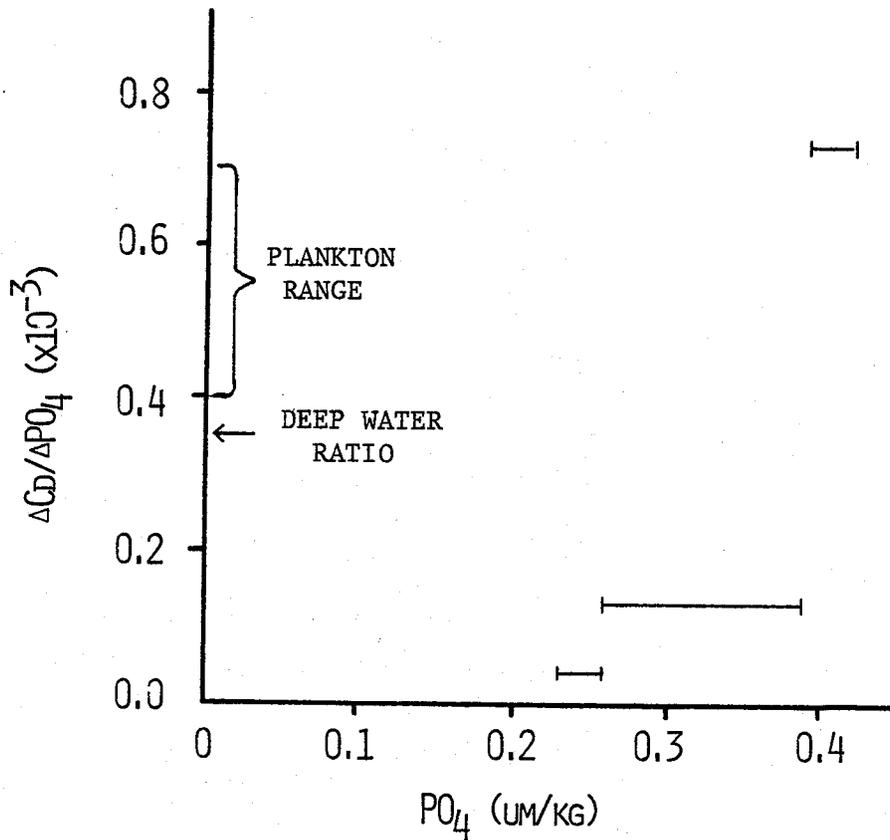
A) Dissolved Cd vs.  $PO_4$  (Bruland, 1980).

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

A



B



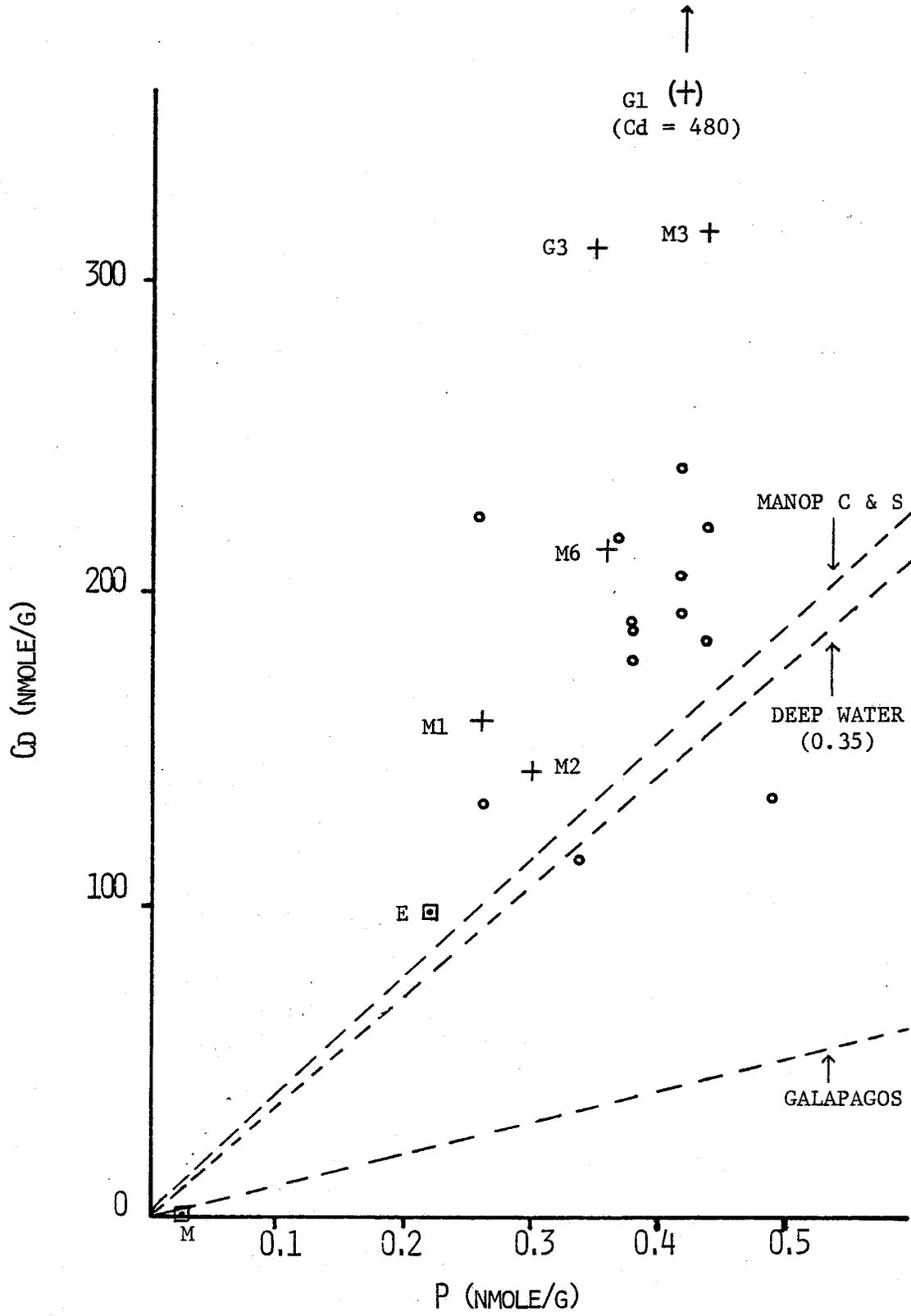
Martin et al.(1976) are plotted in Fig. IV-4. It can be seen that in nearly all cases, the ratio of Cd to P (generally  $0.4$  to  $0.7 \times 10^{-3}$ ) is well above the deep water dissolved ratio ( $0.35 \times 10^{-3}$ ). The plankton samples from MANOP sites C and S are from an oligotrophic environment 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).

V-4. BIOGENIC PARTICULATE TRACE ELEMENT FLUXES

Marine geochemical cycles of the trace elements investigated can be examined in terms of box models describing exchanges between reservoirs which are assumed to be homogeneous. The complexity of such models varies in proportion to the knowledge we have of the distribution of chemical tracers in the system; the rates of inputs, outputs, and internal chemical processes; and the movement of water masses between the reservoirs by advection and diffusion.

The simplest applications of box models to marine systems have used single-reservoir oceans. The total mass of a particular element and its total input or output are used to estimate a residence time of the element (Barth, 1952). Multi-box systems have also been used, with varying success, to describe more detailed distributions (Keeling and Bolin, 1967, 1968; Broecker and Li, 1970; Tsunogai, 1978; Broecker, 1979). These models have usually suffered from a lack of ability to specify sufficient independent parameters to determine a solution.

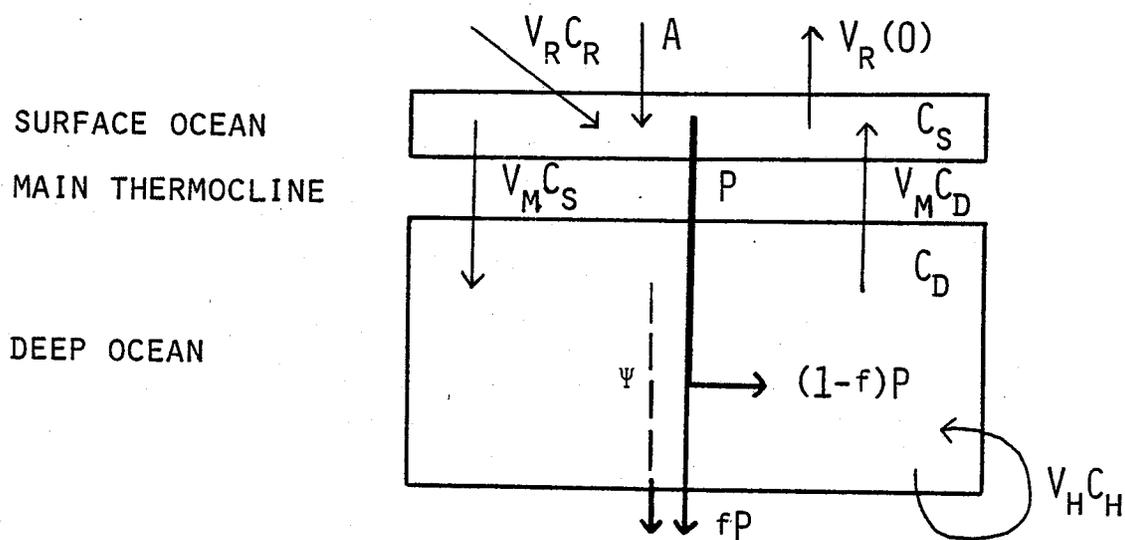
The particulate fluxes driving the vertical segregation of elements involved in the biogeochemical cycles of uptake and regeneration have been interpreted with a simple two-box ocean model with surface and deep reservoirs (Broecker, 1971). The general circulation between the ocean basins (Stommel and Arons, 1960; Reid and Lynn, 1971), coupled with the continuous production of organic matter in the surface ocean, create significant horizontal enrichments of the nutrient elements between the deep Atlantic, Indian, and Pacific oceans. This process has also been modeled in terms of exchanges between two

deep boxes and one surface reservoir (Broecker and Li, 1970). However, new GEOSECS data for the distribution of nutrients and  $^{14}\text{C}$  (Stuiver, 1976; Broecker et al., 1980) show extreme horizontal gradients in the Atlantic "box" and require a rapid flushing time of Atlantic deep water - less than 100 years. Recomputing the parameters of the model, applied to major chemical tracers, shows that it is unstable with respect to small variations in the choice of average surface and deepwater end-member concentrations. This choice is further complicated by the heterogeneity in the basin. In any case, the deep Atlantic data show almost no signature of chemical processes occurring in-situ. Gradients in properties are dominated by mixing between waters masses of North Atlantic and Antarctic origins.

#### Trace element box model

A simple two-box model will be used as a starting point in the examination of the geochemical cycles. Application of the model involves determining the dissolved distributions, the mixing rates of water between the reservoirs, and the primary input or output fluxes for the elements. The predicted fluxes are then compared with biogenic carrier ratios and independent measurements of fluxes within and between the reservoirs. A schematic representation of the box model used, and the appropriate mass-balance equations are given in Fig. IV-5. The terminology is basically the same as that of Broecker (1971).

Figure IV-5. Two-reservoir ocean model.



SURFACE OCEAN:  $A + V_M C_D + V_R C_R = V_M C_S + P$

$$P = V_M (C_D - C_S) + V_R C_R + A$$

DEEP OCEAN:  $V_M C_S + V_H C_H + (1-f)P = V_M C_D + \Psi$

$$fP + \Psi = V_R C_R + V_H C_H + A$$

- WHERE:
- $C_R$  - RIVER CONCENTRATION
  - $C_S$  - SURFACE MIXED LAYER CONCENTRATION
  - $C_D$  - DEEP OCEAN CONCENTRATION
  - $C_H$  - CONCENTRATION IN HYDROTHERMAL INPUT
  - $V_M$  - VOLUME OF WATER EXCHANGED BY MIXING AND ADVECTION
  - $V_R$  - RIVER WATER VOLUME
  - $V_H$  - HYDROTHERMAL VOLUME
  - $A$  - ATMOSPHERIC FLUX
  - $P$  - PARTICULATE FLUX OUT OF MIXED LAYER
  - $f$  - FRACTION OF  $P$  LOST TO THE SEDIMENTS
  - $\Psi$  - SCAVENGING (OR PRECIPITATION) FLUX FROM DEEP OCEAN

### Dissolved distributions

The horizontal heterogeneity of the deep-ocean nutrients and trace elements must be considered when choosing an average deep-reservoir composition. The concentrations in the deep northeast Pacific are not representative of the average ocean and using these values for biologically-cycled elements will overestimate the flux required to maintain their deep enrichment. A volume-weighted factor of 1:4 will be used to average deep Atlantic and Pacific+Indian deep-ocean concentrations (Broecker and Li, 1970). At all Pacific stations where plankton were collected, standard hydrographic, nutrient, and trace element profiles of Cu, Ni, and Cd were determined. These are combined with GEOSECS trace element profiles determined at MIT, and with others from the literature, to give estimates of the oceanic concentration of these elements in the surface and deep reservoirs.

### Reservoir mixing rates.

The volume rate of exchange between the deep and surface reservoirs has generally been estimated using versions of a similar two-layer box model applied to  $^{14}\text{C}$  distributions (Broecker et al., 1960; Broecker and Li, 1970). The early models assumed that the  $^{14}\text{C}$  mixed into the deep ocean was derived from the warm surface layer and was equilibrated with the atmosphere. More detailed data on the hydrography of the Atlantic, Antarctic, and Pacific oceans obtained during the GEOSECS program, emphasize the thermohaline mechanism of deep-water formation from cold, high-latitude surface water which has not equilibrated isotopically with atmospheric  $^{14}\text{CO}_2$  (Stuiver, 1976).

The correction in the  $^{14}\text{C}$  end-member results in a significant lowering of the estimated flushing times for the deep Atlantic ( $\leq 100$  years) and Pacific ( $\leq 900$  years, Broecker, 1979). One of the major sites of deep-water formation, the Weddell Sea, does not reach atmospheric equilibrium and carries very little new  $^{14}\text{C}$  to contribute to the isotopic-flushing time (Weiss et al., 1979). Therefore, the replacement time for water in the deep ocean may be lower by another 30%. Physical mixing parameters based on different elements that may have a variety of boundary conditions must, therefore, be used with caution. Biological production in the high-latitude regions is generally light-limited, so the concentration of the biologically cycled elements remains high - out of "equilibrium" with normally-depleted surface waters. The  $^{14}\text{C}$  and nutrient boundary errors tend to cancel each other out, so water exchange rates based on  $^{14}\text{C}$  will be used as first-order estimates of those carrying the nutrients and trace elements. A  $^{14}\text{C}$  residence time of 930 years (Broecker, 1979) and a mean deep-reservoir thickness of 3200 meters yield a mixing flux,  $V_m$ , of 3.5 meters/year.

#### Primary inputs and outputs

I will consider rivers, atmospheric deposition, and hydrothermal circulation as the only primary inputs for the elements studied. In most cases, rivers will be the only important source. Estimation of the magnitude of all of these fluxes can be extremely difficult and, in the case of many of the trace elements, is currently impossible.

The flux of river water to the oceans,  $V_r$ , is taken to be 10.3 - 12.7 cm/year, distributed over the entire surface area of the oceans (Baumgartner and Reichel, 1975; Korzun et al., 1974). The composition of this flow,  $C_r$ , is poorly known - its estimation involving extrapolation from very few data of questionable coverage and quality (Livingstone, 1963; Martin and Maybeck, 1979). Problems include separation of particulate from dissolved materials, contamination of most of the samples, estimation of pre-anthropogenic levels, and characterization of physical, chemical, and biological processes at the estuarine interface which affect the eventual transport of elements into the open ocean. Therefore, the river flux, although the dominant input for most elements, must be given carefully guarded weight in consideration of the rest of the trace elemental cycles.

Atmospheric inputs of trace elements,  $A$ , are even more difficult to estimate and relatively few attempts to do so have been published. Most of the higher-quality atmospheric particulate estimates have been made over the Atlantic Ocean. These might be biased by the high density of land masses surrounding the Atlantic, compared to that around the Pacific Ocean. Flux estimates used for this model will generally be taken from Wallace et al. (1977) and Buat-Menard and Chesselet (1979). Estimates of the percentage of the total input which is soluble in the surface reservoir will be taken from leaching experiments published by Hodge et al. (1978).

Estimates of hydrothermal inputs of minor elements,  $V_h C_h$ , will be taken from data collected at vents along the Galapagos and East Pacific Rise spreading centers (Edmond et al., 1980a). A great deal of

uncertainty exists in the extrapolation of the minor element fluxes from these systems due to the effects of the subsurface mixing on the removal of high-temperature mobilized elements to secondary precipitates (Edmond et al., 1980b).

The only output considered in the model is through burial in the sediments. The global inventory of sediments - both in composition and accumulation rate is not well known and the separation of the various genetic inputs of the bulk material is very difficult (Goldberg and Arrhenius, 1958; Price and Calvert, 1970; Krishnaswami, 1976; Heath and Dymond, 1977). One of the major motivations in the study of the biogenic trace element cycles is to establish the nature and magnitude of the biogenic inputs to the sedimentary inventory independently, so other inputs such as hydrothermal and authigenic precipitates can be quantified.

#### Internal fluxes

Several other estimates of chemical fluxes within the marine system can be used in comparison to the predicted box model fluxes. The relative magnitude of primary production can be measured and global inventories of carbon fixation rates have been published (Koblentz-Mishke et al., 1970; Platt and Subba Rao, 1973). These will be used to make first-order estimates of the total production of biogenic particulate carriers. The marine productivity estimates generally range between 550 and 650  $\mu\text{mole C/cm}^2\text{-year}$  averaged over the area of the oceans ( $3.62 \times 10^{18} \text{ cm}^2$ ). It has been recognized that the mixing-flux of dissolved  $\text{NO}_3$  accounts for only 20-25% of the total amount of N fixed

into particles (Epply and Peterson, 1979). The balance is made up with recycled organic-N and  $\text{NH}_3$  released from the plankton by rapid heterotrophic activity in the surface reservoir. This primary  $\text{NO}_3$  flux results in an estimate of "new production" which is approximately  $110 \mu\text{mole C/cm}^2\text{-year}$ . Trace elements which are rapidly recycled with P and N in the surface layer (Cd, Ni, Mn) may be transported out of the mixed layer in proportion to this "new productivity" flux. Elements which are fixed into biogenic particles but remain in the particles during this cyclic process (Cu, Zn, Ba, Fe) could be enriched in the resulting flux to a level proportional to the total productivity estimate.

Sediment trap experiments, reported by Deuser and Ross (1980), have demonstrated that the flux of particulate organic carbon to deep traps responds to the surface production rate. Differences in suspended particle concentrations, deep sediment trap collections, and sediment accumulation rates at the Galapagos site also demonstrate a significant dependence on variations in surface productivity (Bishop et al., 1980; Cobler and Dymond, 1980). These deep fluxes should be more closely related to the "new production" estimate than the total surface productivity measurement. For example, the empirical relationship reported by Eppley and Peterson (1979) for open-ocean levels of "new production" is:

$$\text{New/Total production} = 0.0025 \times (\text{Total production} \{ \text{g C/m}^2\text{-year.} \} )$$

The estimates of total production at the Galapagos and MANOP S sites are  $1200$  and  $300 \mu\text{mole C/cm}^2\text{-year}$ , respectively ( $150$  and  $35 \text{ g C/m}^2\text{-year}$ ). The resulting "new production" estimates are  $450$  (38%) and  $25$  (9%)

$\mu\text{mole C/cm}^2\text{-year}$ . These are roughly a factor of 4 above and below the value taken to represent the mean organic carbon flux in the box models. These dramatic differences in surface production are also seen in deep sediment trap fluxes collected at these stations (Cobler and Dymond, 1980; Dymond and Soutar, personal commun.). These fluxes were  $4.5 \text{ mg/cm}^2\text{-year}$  at the Galapagos site and  $0.37 \text{ mg/cm}^2\text{-year}$  at MANOP site S.

The variation of the elemental ratios in the settling particulates, due to differences in the extent of surface recycling of nutrients, has been described in section IV-3 by an enrichment parameter,  $\beta$ . It is reasonable that this parameter would be a function of the ratio of new/total production, although this has not yet been supported by experimental data. The extreme variations in "new production", coupled to related variations in  $\beta$ , must be considered when making direct comparisons of single-site sediment trap data with mean box model estimates.

Because of the definition of the homogeneous reservoirs, box models can not distinguish between chemical processes occurring throughout the whole reservoir and those concentrated at a boundary. This has been a serious problem in considering the sites of regeneration of the biogenic particulate matter - the deep water column or the surface sediments. Several different independent data and models will be considered to address this specific question. These are: one-dimensional advection-diffusion models of the distribution of dissolved tracers in applicable sections of the deep ocean; comparisons of suspended and settling particulate material with surface sediment

accumulations; and bottom fluxes based on dissolved trace element distributions in sediment pore waters.

Chemical properties of the water in the deep ocean are not homogeneous, as assumed in the box model. Over much of the deep Pacific there are linear relationships between conservative chemical tracers with exponential depth variations. These distributions can be interpreted using a steady-state vertical advection-diffusion model (Wyrski, 1962; Craig, 1969) which has been successfully applied to open ocean trace element profiles in the Pacific (Chan et al., 1976; Boyle et al., 1977; Measures et al., 1980). Data for each species are fit to the one-dimensional differential equation:

$$dC/dz = KC'' - WC' + J = 0$$

where K is a vertical eddy diffusivity; W is the vertical advection velocity; J is an assumed zero-order reaction term; and C is the concentration of the tracer. Rearranging and combining the solutions for a conservative tracer (potential temperature -  $\theta$ ) with the chemical tracer (C) as a function of depth (z) yields:

$$C = a + (J/W)z + b\theta$$

The parameter J/W can be determined by a multiple linear regression of the tracer, C, on z and  $\theta$ . Using estimates of vertical advective velocities derived from the application of these same models to radioactive tracers, the net rate of production or consumption, J, can be derived. Integrated over the depth of the section, these rates give an estimate of the net in-situ reactions which can be compared to the

total deep rate predicted by the box model. The difference between the two estimates can be taken to indicate the magnitude of the deep-reservoir reactions occurring above or below the water column segment treated by the advection-diffusion model. These sites could include the thermocline or the sediment interface. The advection-diffusion models will be applied to major biogenic carrier elements as well as directly to the trace elements, where detailed, high-precision water column profiles are available.

The surface particulate matter and deep regeneration fluxes put constraints on the composition of settling particulate matter. Where applicable, data from fine particles collected by Niskin filtration during the GEOSECS program (Brewer, personal communication) and from larger size fractions collected by large volume in-situ filtration (Bishop et al., 1980) will be discussed in terms of compositional variation with depth.

One of the most active areas of marine geochemical research is the direct collection of the settling particulate flux with interceptor traps. Data from traps deployed at two of the plankton tow sites (Cobler and Dymond, 1980; Dymond and Soutar, pers. commun.) and other open-ocean sites (Knauer et al., 1979; Brewer et al., 1980; Knauer and Martin, 1980; Honjo, 1980) will be examined with respect to the box model-estimated particulate fluxes and sediment accumulation rates. Differences between fluxes measured in deep traps and in surface sediments are taken to represent bottom boundary processes which could include: remineralization and release of dissolved elements (Klinkhammer, 1980); increased scavenging rates of elements in a bottom

nepheloid layer (Spencer et al.,1980); or diagenetic alteration of the sediment column (Berner,1980).

Major Component Elements of the Biogenic Carriers

For the purposes of this geochemical study, the cycles of biogenic particulate material will be traced through the distributions of organic carbon, phosphorus, calcium carbonate, and opal. The box model will first be applied to these major particulate phases and their dissolved remineralization products. The carrier fluxes derived from the model will be checked against available independent estimates. These fluxes will then be used with the element:carrier ratios deduced from the leaching experiments to estimate trace element fluxes.

Organic carbon

The input parameters and results of the organic-carbon box model are summarized in Table IV-5. The concentration of dissolved-total  $\text{CO}_2$  is used to follow the regeneration of organic carbon. From isotopic and alkalinity mass balances, the oxidation of organic carbon is taken to account for between 75 and 80% of the total increase in  $\text{CO}_2$  (Kroopnick, 1974; Li et al., 1969). The resulting surface particulate flux calculated from the box model is approximately  $100 \mu\text{mole C/cm}^2\text{-year}$ . The total surface primary production is approximately  $600 \mu\text{mole/cm}^2\text{-year}$ , but estimates at different sites range from  $<100$  to  $>1200 \mu\text{mole/cm}^2\text{-year}$ . The mean "new production" estimate is near  $100 \mu\text{mole/cm}^2\text{-year}$ . This value is in good agreement with the deep  $\Sigma \text{CO}_2$  increase used in the box model. The burial flux of this carbon is only 1-2 % of this surface particulate flux and less than 0.5% of the total primary production (Heath et al., 1977). Sediment trap collections also

Table IV-5. Organic Carbon Cycle

- Primary input fluxes:

Rivers ( $C_r$ ) - Concentration unknown but low compared to marine primary production (DeVoos, 1979).

- Distribution of  $CO_2$ : Surface  $C_s = 2.02 \mu\text{mole/cm}^3$

Deep Atlantic - 2.18

Pacific - 2.43

$C_d = 2.38 \mu\text{mole/cm}^3$

75-80% of change in  $\Sigma CO_2$  is from oxidation of organic carbon  
 $\Sigma CO_2$  (oxidative) =  $(0.75 \text{ to } 0.8) \times (2.38 - 2.02)$   
 $= 0.26 \text{ to } 0.30 \mu\text{mole/cm}^3$

- Box model for surface particulate flux:

$$P_{\text{Corg}} = (350 \text{ cm/year}) \times (0.26 \text{ to } 0.30 \mu\text{mole/cm}^3)$$
$$= 91 \text{ to } 105 \mu\text{mole C/cm}^2\text{-year}$$

- Independent estimates:

Primary production - Total production:  $550\text{-}650 \mu\text{mole/cm}^2\text{-yr}$

"New production":  $95 \text{ to } 125 \mu\text{mole/cm}^2\text{-yr.}$

Sediment traps - Variable flux reflects surface productivity

Approximate percentage of "new production" -

<30% below 500 meters

<10% below 1000

< 2% at bottom.

further loss at sediment surface

Advection-diffusion models of  $O_2$  consumption:

$0.06\text{-}0.14 \mu\text{mole/cm}^3\text{-year}$  or approx.  $32 \mu\text{mole } O_2/\text{cm}^2\text{-year.}$

(@ Redfield  $O_2:C = 138:106$ )  $25 \mu\text{mole C/cm}^2\text{-year.}$

indicate that >95% of the "new production" is probably remineralized before reaching the sediments. Advection-diffusion fits to  $O_2$  profiles in the Pacific indicate consumption rates ranging from .06 to .14  $\mu\text{mole } O_2/\text{liter-year}$ . Using a Redfield ratio for C:O of 106:138, yields an organic-carbon oxidation rate of 20-40  $\mu\text{mole C}/\text{cm}^2\text{-year}$ . The summation of these regeneration fluxes demonstrates that from 60 to 80% of the organic carbon that settles out of the mixed layer is oxidized above 1500 meters depth.

#### Phosphorus

Fluxes of P predicted by the box model are given in Table IV-6. The flux out of the surface reservoir is calculated to be 0.8 - 0.9  $\mu\text{mole P}/\text{cm}^2\text{-year}$ . Using a Redfield ratio of C:P of 106:1 with the total and "new" productivity estimates yields estimates for total and "new" P fluxes of 5.7 and 1.0  $\mu\text{mole}/\text{cm}^2\text{-year}$ , respectively. Suspended particulate samples and sediment trap samples demonstrate a significant loss of P relative to C as particles settle out of the surface layer - with C/P ratios climbing above 800 (Knauer et al., 1979; Bishop et al., 1980; Knauer and Martin, 1980). Advection-diffusion models applied to profiles from stations in the Pacific indicate values for J which range from .03 to .18  $\mu\text{mole P}/\text{cm}^2\text{-year}$  with an average slightly below 0.1. Sediment porewater gradients in P concentrations are usually small indicating an insignificant flux to the deep water (Froelich, 1979; Emerson et al., 1980). The sum of these regeneration fluxes is roughly equivalent to the production and demonstrates that most of the particulate P is remineralized above 1500m and very little

Table IV-6 Phosphorus Cycle

- Primary input fluxes:

Rivers ( $C_r$ ) = 1.0 nmole/cm<sup>3</sup> (Froelich, 1979)

$V_r C_r = 10$  to 13 nmole P/cm<sup>2</sup>-year.

- Distribution of dissolved PO<sub>4</sub>: Surface  $C_s = .05$  pmole/cm<sup>3</sup>

Deep Atlantic - 1.4

Pacific - 2.8

$C_d = 2.5$  pmole/cm<sup>3</sup>

- Box model for surface particulate flux:

$P_p = (350 \text{ cm/year}) \times (2.5 - .05 \text{ nmole/cm}^3) + 13$

$= 0.87 \text{ } \mu\text{mole P/cm}^2\text{-year}$

- Independent estimates:

Primary production -

Total organic C production x Redfield ratio (1:106)

$= 5.7 \text{ } \mu\text{mole P/cm}^2\text{-year}$

from "new production" = 1.0  $\mu\text{mole P/cm}^2\text{-year}$

Sediment traps -

California Current (Knauer and Martin., 1980)	depth	P flux ( $\mu\text{mole/cm}^2\text{-year}$ )
	35m	16
	65	6.6
	150	4.0
	500	.95
	750	.91
	1500	2.4
North Pacific central gyre (Knauer et al., 1979)	75	.51
	575	.10
	1050	.04

Pore water fluxes - low ( $\leq 0.01 \mu\text{mole/cm}^2\text{-year}$ ; Froelich, 1979)

Advection-diffusion models for PO<sub>4</sub> - 0.03 to 0.18  $\mu\text{mole/cm}^2\text{-yr}$   
(average - 0.1)

survives transit to the sediments.

### Calcium Carbonate

The distribution and fluxes of  $\text{CaCO}_3$  in terms of the two-box ocean are outlined in Table IV-7. Even for the major element, Ca, the primary river and hydrothermal fluxes are uncertain by at least +30%. However, as in the case of P, the cyclic flux required to maintain even the slight deep enrichment of Ca is the dominant fraction of the total particulate flux out of the surface ocean. The box model predicts that this flux should range between 24 and 48  $\mu\text{mole Ca/cm}^2\text{-year}$ . The relatively large error has its source in the high variability of the surface water concentration of salinity-normalized Ca (Horibe et al., 1974; Brewer et al., 1975; Shiller and Gieskes, 1980). A total  $\text{CaCO}_3$  production of 200  $\mu\text{mole Ca/cm}^2\text{-yr.}$  is estimated based on the total primary production of 550-650  $\mu\text{mole C/cm}^2\text{-year}$  with a mean Ca:C ratio of 0.33 (Lisitzin, 1972). The same estimate based on the "new production" number is 33  $\mu\text{mole Ca/cm}^2\text{-year}$ , which is again in agreement with the box model prediction. Honjo (1980) has reported that trapped material shows little signs of dissolution within the water column - even in the highly corrosive deep Pacific; however, the measured flux in these and other Pacific traps seems to be a factor of 2 to 4 below the estimated surface production. Advection-diffusion models of alkalinity profiles indicate highly variable remineralization within the water column and do not constrain the site of dissolution (Edmond, 1974). A significant decrease in  $\text{CaCO}_3$  flux occurs between the deep traps and bottom accumulations at the Galapagos and MANOP sites. This is due to the



dissolution of the  $\text{CaCO}_3$  at the sediment surface.

### Opal

The geochemical box model of biogenic Si is outlined in Table IV-8. The input fluxes ( $2.3\text{-}2.5 \mu\text{mole}/\text{cm}^2\text{-yr.}$ ) are again a small fraction of the total particulate flux ( $43\text{-}47 \mu\text{mole}/\text{cm}^2\text{-yr.}$ ) needed to drive the deep-water enrichment. The particulate Si formed can be estimated using the primary production and a Si/C ratio of 0.42 (Lisitzin, 1972). The total production is  $250 \mu\text{mole}/\text{cm}^2\text{-year}$  and the "new production" equivalent is  $42 \mu\text{mole}/\text{cm}^2\text{-year}$ . The lower value is closer to that predicted by other estimates and, if the Si:C ratio is correct, demonstrates that a large fraction of the Si uptake by organisms is recycled in the surface ocean. Using the box model results from  $\text{CaCO}_3$ , with the observed ratio between  $A_t$  and Si (Edmond, 1974), predicts a flux between 48 to  $76 \mu\text{mole Si}/\text{cm}^2\text{-year}$ . Sediment traps again reflect the variability of surface production and significant remineralization in the water column - collecting several tens of percent of the opal predicted from "new production". Bottom dissolution is also indicated in the difference between the deep trap and surface sediment accumulations. This is consistent with porewater fluxes of between 1 and  $10 \mu\text{mole}/\text{cm}^2\text{-year}$  (Hurd, 1973; Schink et al., 1975). Advection-diffusion fits for the Pacific generally result in a value of J between 10 and  $20 \mu\text{mole}/\text{cm}^2\text{-year}$ . The quality of the fits is poor and the validity of the one-dimensional model applied to Si distributions is questionable since strong horizontal gradients exist in the north Pacific, apparently driven by the bottom dissolution flux (Edmond et al, 1979c).

Table IV-8. Biogenic Si Cycle

- Primary input fluxes:

Rivers ( $C_r V_r$ ) = 1.35 to 2.0  $\mu\text{mole Si/cm}^2\text{-year}$  (Demaster, 1979).

Hydrothermal ( $C_h V_h$ ) = 0.8  $\mu\text{mole Si/cm}^2\text{-year}$  (Edmond et al., 1979a)

- Distribution of dissolved Si: Surface  $C_s = 1 \text{ nmole/cm}^3$

Deep Atlantic - 30

Pacific - 150

$C_d = 126 \text{ nmole/cm}^3$

- Box model for surface particulate flux:

$$P_{\text{Si}} = (350 \text{ cm/year}) \times 126 \text{ nmole/cm}^3 + 1.7 \mu\text{mole/cm}^2\text{-yr.}$$
$$= 45 \mu\text{mole Si/cm}^2\text{-year.}$$

- Independent estimates:

Primary production - (neglects radiolaria)  
assume Si:C = 0.42 (Lisitzin, 1972)

Total production - 250  $\mu\text{mole Si/cm}^2\text{-year}$

"new" production - 42  $\mu\text{mole Si/cm}^2\text{-year}$

Empirical relation between  $A_t$  and Si implies regeneration ratio = 2:

2 x box model Ca flux = 48 to 76  $\mu\text{mole/cm}^2\text{-year}$ .

Sediment traps - Strong function of surface production:

Deep traps collect between 15-30% of "new" production.

Differences between traps and sediments indicate continued dissolution.

Porewaters: Fluxes range between 1 - 10  $\mu\text{mole Si/cm}^2\text{-year}$   
(Hurd, 1973; Schink et al., 1975)

Advection-diffusion models for Si regeneration:

May be invalid due to strong horizontal gradients, especially in the north Pacific.

The range of J's yield fluxes: 10-20  $\mu\text{mole Si/cm}^2\text{-year}$ .

### Biogenic Fluxes and Trace Element Cycles

It is clear from the above discussion, that the box model predicts fluxes of biogenic elements which are entirely consistent with direct independent measurements. Especially notable is the agreement based on the estimates of "new production" as representing the initial flux of biogenic carriers out of the mixed layer. These can now be coupled with the plankton-trace element leaching ratios and the dissolved distributions to examine the role of biogenic particles in the specific trace element cycles.

#### Cadmium

A summary of the distribution and fluxes of Cd estimated from various sources is presented in Table IV-9. A difficulty experienced in describing the Cd cycle, which is common to all of the trace elements, is that the nature and magnitude of the primary inputs are poorly known. The river flux used for Cd is based solely on estimates from the Amazon river (Boyle, personal commun.), and probably represents only the order of magnitude of the flux - at best. The atmospheric flux is based on Atlantic Ocean air concentration measurements near Bermuda, coupled with a model for the rate of washout-deposition (Wallace et al., 1977). The Pacific atmospheric fluxes are probably much lower (Bruland, 1980).

The distribution of dissolved Cd in the Pacific is relatively well known (Boyle et al., 1976; Bruland et al., 1978; Bruland 1980). The Atlantic value is taken from Bender and Gagner (1976) and from a

Table IV-9. Cadmium Cycle

- Primary input fluxes:

Rivers -  $C_r = 0.1 - 0.6 \text{ nmole/cm}^3$  (Amazon; Boyle pers. commun.)

$$C_r V_r = .001 \text{ to } .006 \text{ nm/cm}^2\text{-year}$$

Atmospheric -  $A \leq .017 \text{ nm/cm}^2\text{-year}$  (Wallace et al., 1977)  
(80% soluble)

- Distribution of dissolved Cd: Surface  $C_s \leq 0.01 \text{ pmole/cm}^3$

Deep Atlantic - 0.35

$$C_d = 0.9 \text{ pmole/cm}^3$$

Pacific - 1.0

- Box model for surface particulate flux:

$$P_{Cd} = (350 \text{ cm/year}) \times (0.9 \text{ pmole/cm}^3) + (0.02 \text{ nmole/cm}^2\text{-year})$$
$$= 0.34 \text{ nmole Cd/cm}^2\text{-year}$$

- Independent estimates:

Using carrier ratios -

Total organic matter as P flux ( $0.87 \text{ } \mu\text{mole/cm}^2\text{-yr}$ );  
plankton Cd/P ratios -  $0.4-0.7 \times 10^{-3}$ :  
Cd flux =  $0.35-0.61 \text{ nm/cm}^2\text{-year}$ .  
(to balance deep enrichment requires  $\beta = 0.5-0.9$ )

$\text{CaCO}_3$  ( $30 \pm 5 \text{ } \mu\text{mole Ca/cm}^2\text{-year}$ );  
ratio of Cd/Ca in forams -  $.025 \times 10^{-6}$ :  
Carbonate carrier flux  $\leq .001 \text{ nmole Cd/cm}^2\text{-year}$ .

Sediment traps - California Current  $15 \text{ nm/cm}^2\text{-yr}$  @ 35 meters;  
(Knauer and Martin, 1980)  $1.4 \text{ nm/cm}^2\text{-yr}$  500 meters.

Advection-diffusion models of deep Cd distribution -  
regeneration of  $0.02-0.05 \text{ nm Cd/cm}^2\text{-yr}$ .

Sediment accumulation of Cd based on P burial flux (Froelich, 1979) -

$$(4 \text{ nmole P/cm}^2\text{-yr}) \times (.35 \times 10^{-3} \{Cd/P\}) = .001-.002 \text{ nmole Cd/cm}^2\text{-yr.}$$

(consistent with lowest primary input estimates.)

preliminary profile from GEOSECS station 54, analysed by F. Sclater at MIT.

The magnitudes of the various components of the total particulate Cd flux demonstrate that, as in the case of P, the cyclic component completely dominates the total. The product of the Cd/P ratio in plankton and the box model flux of P predicts a Cd flux which is too high compared with the flux calculated using the box model for dissolved Cd. A fraction of the total Cd measured in the plankton samples must be recycled more rapidly than P, such that the elemental ratio of the particulate flux into the deep box is lower by a factor of  $\beta$ . To balance the box-model Cd flux with the C:P carrier flux requires a value of  $\beta$  between 0.5 and 0.9. The sediment trap data from Knauer and Martin (1980), presented in Table IV-9, also confirms the transport of particulate phases which have lower Cd/P ratios than the surface plankton.

If the carrier model is extended to the sediments, then a rough estimate of the Cd sedimentation rate can be derived from the rate of P burial with organic matter ( $4 \text{ nm P/cm}^2\text{-yr}$ ; Froelich, 1979). This is certainly subject to large errors since relatively small differences in the total regeneration ratio create large variations in the residual ratio delivered to the sediments. The only independent estimate available is a set of porewater Cd and P analyses collected during the MANOP program (G. Klinkhammer, pers. commun.). In these samples the Cd:P ratio ranges from 0.4 to  $0.8 \times 10^{-3}$ . Taking an overall range in ratios between  $0.35 \times 10^{-3}$  (water column) to  $0.8 \times 10^{-3}$  (porewater) gives sediment output fluxes of 0.001 to  $0.003 \text{ nm Cd/cm}^2\text{-yr}$ . These are

consistent with the lower river input estimates and support the contention that the estimate of atmospheric input is too high.

### Nickel

The box model geochemical cycle and carrier fluxes for Ni are outlined in Table IV-10. Again, the river input estimates are limited and the atmospheric value is derived from the Atlantic stations of Wallace et al. (1977). Edmond et al. (1979b) have shown that hydrothermal circulation can act as a source or sink for Ni and other sulfide-forming transition elements. Direct, high temperature effluents to the ocean bottom (ie. - 21<sup>o</sup>N on the EPR) could contribute a significant input of metals including Ni. However, the precipitation of secondary metal sulfides within more complex ridge-crest circulation systems (ie. - Galapagos vents) appears to remove metals from seawater. The global significance of this source (sink) to the deep ocean reservoir remains uncertain - but this deep primary flux only indirectly affects the estimation of the surface particulate flux through the value of  $C_d - C_s$ .

The box model calculations predict that approximately 90-95% of the total particulate Ni leaving the surface is regenerated. An inventory of the carrier fluxes demonstrates that  $CaCO_3$  and opal fluxes are probably insignificant. The organic flux represented by the bulk plankton Ni/P ratio and the total P flux is too low to account for the deep-water enrichment. Using a value of 2.4 for  $\beta$ , derived from the leaching experiments, brings the total estimated carrier flux significantly closer to the box model value. The Ni:P ratio in the

Table IV-10. Nickel Cycle

- Primary input fluxes:

Rivers -  $C_r = 9 \text{ pmole/cm}^3$  (Sclater et al., 1976)

$$V_r C_r = 0.11 \text{ nmole/cm}^2\text{-year.}$$

Atmospheric-  $A = 0.04 \text{ nmole/cm}^2\text{-year}$  (Wallace et al., 1977)  
(40% soluble)

- Distribution of dissolved Ni: Surface  $C_s = 2 \text{ pmole/cm}^3$

Deep Atlantic - 7

Pacific - 10  $C_d = 9 \text{ pmole/cm}^3$

- Box model for surface particulate flux:

$$P_{Ni} = (350 \text{ cm/year}) \times (9 - 2 \text{ pmole/cm}^3) + 0.15 \text{ nmole/cm}^2\text{-yr.}$$
$$= 2.7 \text{ nmole/cm}^2\text{-year.}$$

- Independent flux estimates:

Using carrier ratios -

Total organic matter as P flux ( $0.87 \text{ } \mu\text{mole P/cm}^2\text{-year}$ );  
plankton Ni/P ratio -  $0.6\text{-}1.1 \times 10^{-3}$ ;

Ni flux =  $0.5\text{-}1.0 \text{ nmole Ni/cm}^2\text{-year}$ .  
(for  $\beta = 2.4$ , Ni flux =  $1.2\text{-}2.3 \text{ "}$  )

$\text{CaCO}_3$  ( $30 \pm 5 \text{ } \mu\text{mole Ca/cm}^2\text{-year}$ );  $-6$

Ni/Ca ratio in forams -  $0.4 \times 10^{-6}$ ;

Carbonate carrier flux =  $0.01 \text{ nmole Ni/cm}^2\text{-year}$ .

Opal ( $45 \text{ } \mu\text{mole Si/cm}^2\text{-year}$ );

Ni/Si ratio (unwashed diatoms) -  $1.3 \times 10^{-6}$

Opal carrier flux =  $0.06 \text{ nmole Ni/cm}^2\text{-year}$ .

Sediment traps: Site S trap -  $0.17 \text{ nmole/cm}^2\text{-yr.}$   
(Dymond and Soutar, pers. com.) sediment -  $0.17 \text{ "}$

Galapagos trap -  $4.7 \text{ nmole/cm}^2\text{-yr.}$   
(Cobler and Dymond, 1980) sediment -  $12 \text{ "}$

Advection-diffusion modeled regeneration -  $0.6 \pm 0.4 \text{ nmole Ni/cm}^2\text{-yr.}$

Porewater fluxes at sites C and S  $< 0.2 \text{ nmole Ni/cm}^2\text{-yr.}$   
(Klinkhammer, personal communication)

material settling into the deep ocean must be higher than the measured plankton values by a factor of 2-4. Ni water column profiles show a component of shallow regeneration but the surface reservoir recycling must be significantly less than that for P.

The site of regeneration of the deep Ni flux can be examined from several independent estimates. The water column profiles and rapid release of Ni with P in the leaching experiments suggest that Ni begins to be regenerated early after the particles settle out of the surface ocean. The regenerative flux calculated for much of the deep reservoir by the application of advection-diffusion models varies from site to site but ranges from 10 to 50% of the total surface flux. The pore water flux appears to be  $\leq 10\%$  of the surface flux at the two stations examined (Klinkhammer, unpublished data), so the balance requires that 40-90% of the surface flux be regenerated above 1500 meters.

### Manganese

The distribution and biogenic particulate components of the Mn geochemical cycle are outlined in Table IV-11. The obvious differences between the dissolved distribution of Mn (Klinkhammer and Bender, 1980) and those of Ni and Cd demonstrate that surface uptake and regeneration are not significant in controlling the concentration of dissolved Mn. Although the surface concentration is higher than the deep concentration, the primary inputs to the surface layer - rivers and atmospheric deposition - require a significant total particulate flux from the surface. In the case of Mn this total flux is essentially determined by the magnitude of these primary inputs (and

Table IV-11. Manganese Cycle

- Primary input fluxes:

Rivers-  $C_r = 0.13 \text{ pmole/cm}^3$  (Bender et al., 1977)

$V_r C_r = 1.7 \text{ nmole/cm}^2\text{-year.}$

Atmospheric-  $A = 0.8 \text{ nmole/cm}^2\text{-year.}$  (Wallace et al., 1977)  
(30-50% soluble)

Hydrothermal-  $V_h C_h = 16-40 \text{ nmole/cm}^2\text{-year}$  (Edmond et al., 1979b)

- Distribution of dissolved Mn: Surface  $C_s = 0.8-3.0 \text{ pmole/cm}^3$

Deep Atlantic - 1.8

Pacific - 0.2-1.0  $C_d = 0.5-1.2 \text{ pmole/cm}^3$

- Box model for surface particulate flux:

$P_{Mn} = (350 \text{ cm/year}) \times (-0.5 \text{ to } -1.0 \text{ pmole/cm}^3) + 2.5 \text{ nmole/cm}^2\text{-yr.}$

$= 2.1 \text{ to } 2.3 \text{ nmole/cm}^2\text{-year.}$  (completely driven by input choices)

- Independent estimates:

Using carrier ratios -

Total organic matter as P flux ( $0.87 \text{ umole P/cm}^2\text{-year}$ );

plankton Mn/P ratios -  $0.35-0.43 \times 10^{-3}$ :

Mn flux =  $0.3 \text{ to } 0.4 \text{ nmole/cm}^2\text{-yr.}$

(with  $\beta = 2$ , Mn flux =  $0.6 \text{ to } 0.8 \text{ "}$ )

$\text{CaCO}_3$  ( $30 \pm 5 \text{ umole Ca/cm}^2\text{-year}$ );  $-6$

ratio of Mn/Ca in forams -  $0.4 \times 10^{-6}$ :

Carbonate carrier flux =  $0.01 \text{ nmole/cm}^2\text{-year.}$

Sediment traps- Site S

trap -  $0.6 \text{ nmole/cm}^2\text{-yr.}$

(Dymond and Soutar, pers. com.)

sediment - 4.2 "

Galapagos

trap -  $430 \text{ nmole/cm}^2\text{-yr.}$

(Cobler and Dymond, 1980)

sediment - 1400 "

sensitive to errors in their estimate), whereas for the biogenically cycled elements, the regenerative flux from upwelling largely determines the particulate flux. Another unique component of the total cycle for Mn is the dominant primary flux to the deep reservoir from hydrothermal circulation.

Examination of the organic carrier shows that the plankton ratio, even when modified by a regenerative enrichment of 2 ( $\beta$ ), is insufficient to balance the box model flux. The fluxes by other biogenic carriers are also low. The dissolved Mn maxima coincident with the  $O_2$  minima in Pacific profiles (Klinkhammer and Bender, 1980; Landing and Bruland, 1980), has been ascribed to horizontal diffusion of mobilized sediment-Mn, equilibrium with a suspended Mn-oxide phase, and regeneration of biogenic Mn during the remineralization of organic matter. The Mn/P ratio seen in the thermocline at several Pacific stations is similar to that measured in the plankton samples, and would be consistent with the rapid release of Mn seen during the leaching experiments. However, in other stations the Mn maximum is absent and, in the more strongly reducing environments of the eastern tropical Pacific profiles, the Mn:P ratio is much larger. These variations imply that the feature is probably not controlled by simple in-situ remineralization of organically bound Mn.

Our inability to account for the required surface particulate flux indicates that either a scavenging mechanism, which is also efficient in removing the large deep-water hydrothermal input, is functioning to rapidly enrich the settling material near the surface or that the estimate of primary surface inputs may be too high. The sediment trap

fluxes further emphasize secondary enrichment processes with deep flux variations ranging over nearly 3 orders of magnitude.

### Copper

The parameters and fluxes used in the box model for the biogeochemical cycle of Cu are given in Table IV-12. Again, the estimates of the primary river input are based on the Amazon concentration reported by Boyle et al.(1977). The atmospheric flux, as estimated from Wallace et al.(1977), could be on the same order of magnitude as the river input. These primary inputs, coupled with the concentration data for the Pacific and Atlantic (Boyle et al.,1977; Moore,1978) can be used to estimate an approximate Cu residence time of 6000 years.

The particulate flux required to maintain the deep enrichment of Cu is accounted for by using the surface Cu/P carrier ratio, modified by an enrichment factor,  $\beta$ , of 3. This factor is consistent with the relative release of Cu with respect to P from the plankton during the seawater leaching experiments. Examination of the other possible carriers demonstrates that  $\text{CaCO}_3$  is probably insignificant and that opal may carry up to 10% of the required flux.

The deep ocean distribution of Cu is unique among those of the other trace elements studied. Although it has a deep enrichment over the surface waters, it is continuously scavenged throughout the water column - requiring its regeneration site to be at the sediment interface (Boyle et al.,1977). This behavior can be verified with several independent flux estimates and is consistent with the leaching

Table IV-12. Copper Cycle

- Primary input fluxes:

Rivers-  $C_r = 18 \text{ pmole/cm}^3$  (Boyle et al., 1977)

$V_r C_r = 0.2 \text{ nmole/cm}^2\text{-year.}$

Atmospheric-  $A = 0.15 \text{ nmole/cm}^2\text{-yr}$  (Wallace et al., 1977)  
(20% soluble)

- Distribution of dissolved Cu: Surface  $C_s = 1-1.5 \text{ pmole/cm}^3$

Deep Atlantic - 2

$C_d = 4.0 \text{ pmole/cm}^3$

Pacific - 4-5

- Box model for surface particulate flux:

$P_{Cu} = (350 \text{ cm/year}) \times (2.5 \text{ to } 3.0 \text{ pmole/cm}^3) + 0.35 \text{ nmole/cm}^2\text{-yr.}$   
 $= 1.2-1.4 \text{ nmole Cu/cm}^2\text{-year.}$

-Independent estimates:

Using carrier ratios -

Total organic matter as P flux ( $0.87 \text{ } \mu\text{mole/cm}^2\text{-year}$ );  
plankton Cu/P ratio -  $0.5-0.6 \times 10^{-3}$ :  
Cu flux =  $0.44-0.52 \text{ nmole/cm}^2\text{-year.}$   
(with  $\beta = 3.4$ , Cu flux =  $1.5-1.8 \text{ "}$ )

$\text{CaCO}_3$  ( $30 \pm 5 \text{ } \mu\text{mole Ca/cm}^2\text{-yr}$ );  
ratio of Cu/Ca in forams -  $0.3 \times 10^{-6}$ :  
Carbonate carrier flux =  $0.01 \text{ nmole Cu/cm}^2\text{-year.}$

Opal ( $45 \text{ } \mu\text{mole Si/cm}^2\text{-year}$ );  
ratio of Cu/Si in unwashed diatoms -  $3.8 \times 10^{-6}$ :  
Opal carrier flux =  $0.17 \text{ nmole Cu/cm}^2\text{-year.}$

Sediment traps - Site S trap -  $0.91 \text{ nmole/cm}^2\text{-year}$   
(Soutar, 1980) sediment -  $0.25 \text{ "}$

Galapagos trap -  $5.2 \text{ nmole/cm}^2\text{-year}$   
(Cobler and Dymond, 1980) sediment -  $4.6 \text{ "}$

Porewater fluxes - (Klinkhammer, 1980, personal communication)

MANOP M, H, S -  $1-2 \text{ nmole/cm}^2\text{-year}$   
MANOP C - 6 "

Fluxes estimated from advection-diffusion models - scavenging:

Pacific stations range from  $0.3 \text{ to } 1.7 \text{ nmole/cm}^2\text{-year.}$

behavior of the surface plankton.

The sediment trap collections at site S and G demonstrate: 1) total Cu fluxes which are similar to the box model estimates; 2) flux variations which parallel the surface productivity difference between sites; 3) fluxes which are larger than the sediment accumulations below them due to the release of Cu at the sediment interface.

Pore water concentrations of Cu measured by Klinkhammer(1980; personal communication) confirm the required regeneration and flux of Cu from the surface sediments at several Pacific MANOP sites. These fluxes are roughly equivalent to the particulate flux out of the surface ocean. Even though the  $\text{CaCO}_3$  phase does not carry significant Cu, the carbonate sediments at site C give a much higher flux of Cu than the other Pacific sediments. This is consistent with the reported correlation of Cu with Ca in marine sediments (Turekian and Imbrie, 1966; Burnett, 1971).

There have been an increasing number of dissolved Cu profiles available from the Pacific (Boyle et al., 1977; Bruland, 1980; several unpublished profiles from the GEOSECS, Hydrothermal, and MANOP research at MIT). The application of steady-state, one-dimensional advection-diffusion models to these data shows systematic variations in Cu scavenging rates which contribute from 25 to 100% of the surface particle flux to the total deep flux. The scavenging rate should be a function of the flux of particles passing through the water column. Deuser and Ross(1980) have demonstrated a variation in total organic flux - even at 3200 meters - which is driven by the surface production rate. If these particles are acting as (or are related to) the primary

scavengers, then the water column uptake of Cu should also vary with the regional mean productivity. Estimates of primary productivity from Koblentz-Mishke et al.(1970) and a related parameter -  $PO_4$  at 100 meters (Reid, 1962) - have been compared to the values of  $J/w$  derived from the Pacific profiles and are shown together in Fig. IV-6. There is clearly a correlation between the scavenging rate and these upper ocean properties which determine the deep-ocean flux of organic particulate matter. Due to the magnitude of the uncertainties involved in these data and models, it is impossible at this point to further quantify this relationship. This result emphasizes the importance of the areas of high productivity in driving much of the total vertical transport of elements in the oceans. This is caused by the combination of the rapid vertical mixing of nutrients which drive the high rates of particulate production, the rapid settling of this organic material, and the increased scavenging of specific elements throughout the water column by these particles.

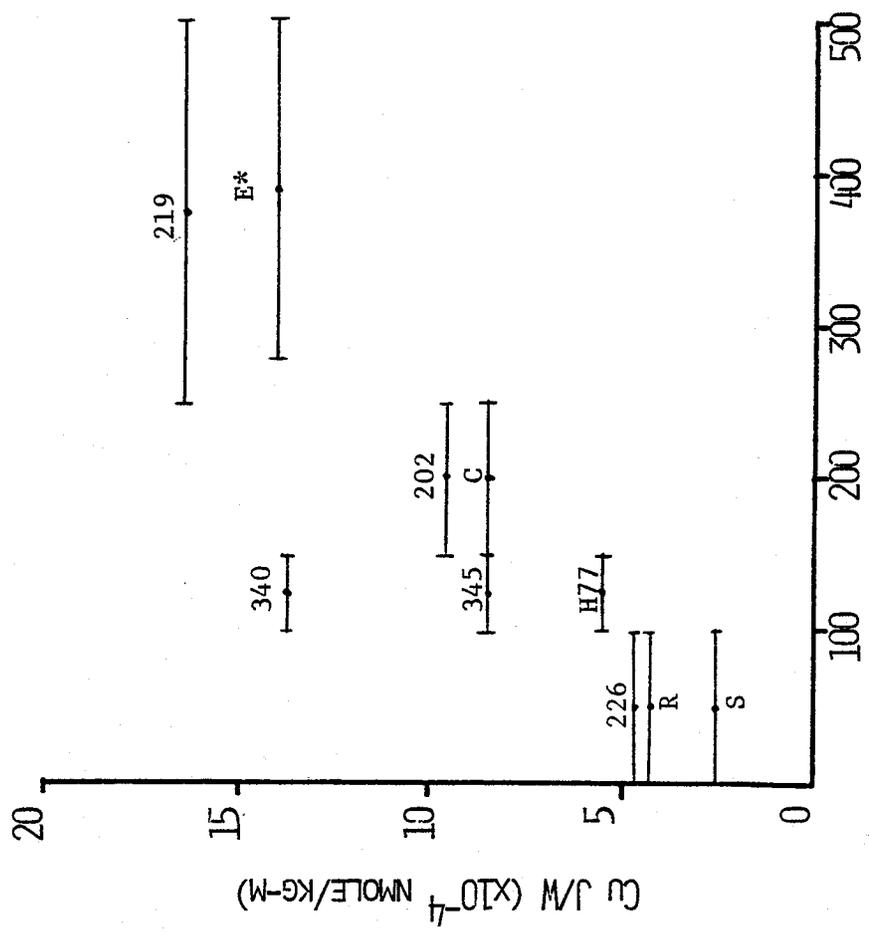
### Zinc

The biogeochemical fluxes of Zn are outlined in Table IV-13. All of the river input estimates yield Zn residence times which are  $\leq 1000$  years. As discussed by Bruland (1980), this is inconsistent with an element which shows significant regeneration along with organic material within the deep ocean. Output flux estimates based on crude sediment inventories (Turekian and Wedepohl, 1961) range between 0.2 and 0.4 nm Zn/cm<sup>2</sup>-year which would result in more reasonable residence times of at least several thousand years.

Figure IV-6. Surface productivity estimates vs. scavenging rates at Pacific stations.

(E\* - Estimated from Atlantic sediment trap data of Brewer et al., 1980)

A



B

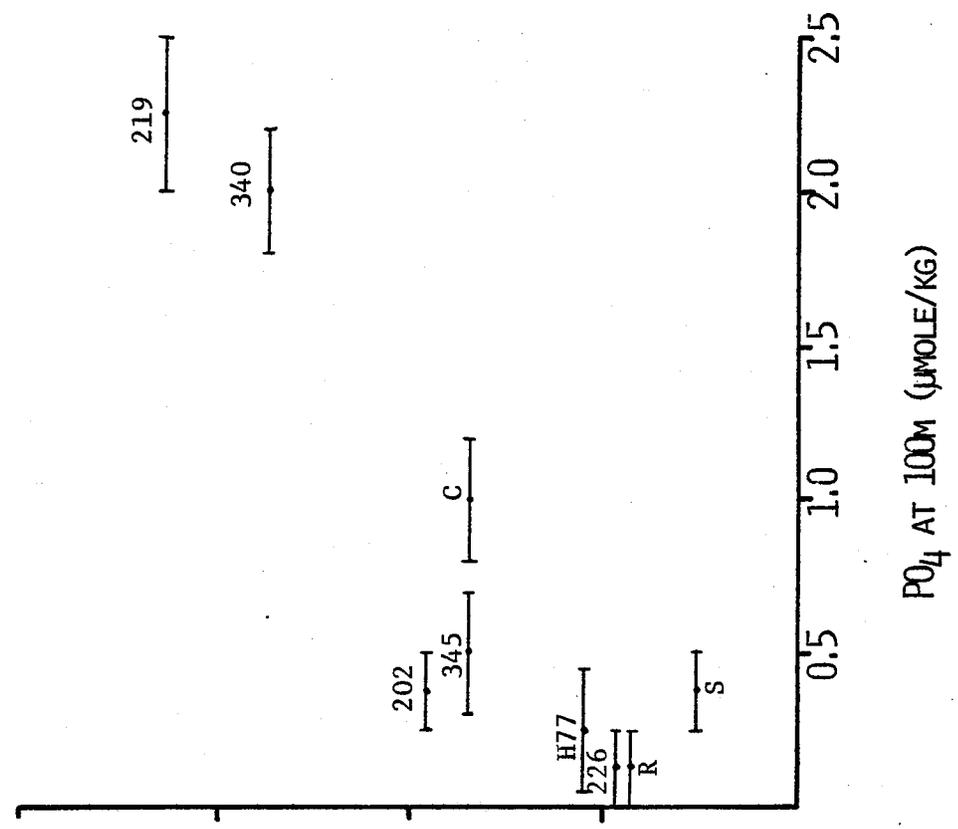


Table IV-13. Zinc Cycle

-Primary input fluxes:

Rivers-  $C_r = (\text{unknown, probably } < 0.1 \text{ nmole/cm}^3)$

Atmospheric-  $A = 0.33 \text{ nm/cm}^2\text{-year}$  (Wallace et al., 1977)  
(50% soluble)

(sum of river and atmosphere flux probably  $\leq 1 \text{ nmole Zn/cm}^2\text{-year}$ )

Hydrothermal - maximum possible value -  $4 \text{ nmole/cm}^2\text{-year}$   
(K. VonDamm, personal communication)

- Distribution of dissolved Zn: Surface  $C_s = 0.8 \text{ pmole/cm}^3$

Deep Atlantic -(1.6)

Pacific - 8.2  $C_d = 7 \text{ pmole/cm}^3$

- Box model for surface particulate flux:

$$P_{Zn} = (350 \text{ cm/year}) \times (7 \text{ pmole/cm}^3) + (?)$$

$$= 2.4 \text{ nmole/cm}^2\text{-year} \quad (+ \text{ unknown primary surface input})$$

- Independent estimates:

Using carrier ratios -

Total organic matter as P flux ( $0.87 \text{ } \mu\text{mole/cm}^2\text{-year}$ );  
plankton Zn/P ratio -  $2-5 \times 10^{-3}$ :

$$\text{Zn flux} = 1.7-4.4 \text{ nmole/cm}^2\text{-year}$$

$\text{CaCO}_3$  ( $30 \pm 5 \text{ } \mu\text{mole Ca/cm}^2\text{-year}$ );  
ratio of Zn/Ca in forams -  $0.5 \times 10^{-6}$ :

$$\text{Carbonate carrier flux} = 0.02 \text{ nmole Zn/cm}^2\text{-year}$$

Opal ( $45 \text{ } \mu\text{mole Si/cm}^2\text{-year}$ );

Ratio of Zn/Si in diatoms -  $1.9-2.6 \times 10^{-5}$ :

$$\text{Opal carrier flux} = 0.9-1.2 \text{ nmole Zn/cm}^2\text{-year.}$$

Sediment traps - Site S trap -  $1.7 \text{ nmole Zn/cm}^2\text{-yr}$   
(Soutar, 1980) sediment - 0.06 "

Galapagos trap -  $7.6 \text{ nmole Zn/cm}^2\text{-yr}$   
(Cobler and Dymond, 1980) sediment - 7.4 "

It can be seen that the range of total organic flux predicted by the P flux carrier ratio in bulk plankton includes the box model value. However, using any significant regenerative enrichment ratio for Zn relative to P creates too much Zn in the settling particles. This problem has not yet been reconciled within the current model. Of the other carriers,  $\text{CaCO}_3$  appears to be insignificant, while opal may carry on the order of 50% of the required flux.

The sediment trap at site S indicates a significant loss of Zn at the sediment interface which is equivalent to the required deep dissolution flux but the sediment traps at the Galapagos show no significant difference from sediment accumulations.

#### Barium

Barium has been studied for many years as a chemical analog for  $^{226}\text{Ra}$  and is one of the first systematically determined trace elements whose distribution indicates involvement in biological cycling (Chow and Goldberg, 1960; Bacon and Edmond, 1972; Chan et al., 1976, 1977). The primary input fluxes and distribution of Ba used in the box model are presented in Table IV-14. The input fluxes are somewhat uncertain due to the desorption of Ba from suspended material in estuaries (Hanor and Chan, 1977; Edmond et al., 1978) and to new estimates of hydrothermal inputs (Edmond et al., 1979a). However, the cyclic flux required by the deep enrichment, completely dominates the total surface particulate flux. Examination of all of the known possible carriers, outlined in Table IV-14, indicates a serious deficit in accounting for the magnitude of the deep Ba enrichment. This unique situation requires

Table IV-14. Barium Cycle

- Primary input fluxes:

Rivers-  $C_r = 0.2-0.37 \text{ nmole/cm}^3$  (Edmond et al., 1978)

$V_r C_r = 2-3 \text{ nmole Ba/cm}^2\text{-year.}$

Hydrothermal-  $V_h C_h = 0.7-1.7 \text{ nmole Ba/cm}^2\text{-year}$   
(Edmond et al., 1979a)

- Distribution of dissolved Ba: Surface  $C_s = 35 \text{ pmole/cm}^3$

Deep Atlantic - 70

Pacific - 150

$C_d = 135 \text{ pmole/cm}^3$

- Box model for surface particulate flux:

$P_{Ba} = (350 \text{ cm/year}) \times (100 \text{ pmole/cm}^3) + 2.5 \text{ nmole/cm}^2\text{-year.}$   
 $= 37 \text{ nmole Ba/cm}^2\text{-year.}$

- Independent estimates:

Using carrier ratios -

Total organic matter as P ( $0.87 \text{ umole P/cm}^2\text{-year}$ );  
ratio of Ba/P in plankton -  $1.4-1.8 \times 10^{-3}$ :  
Ba flux =  $1.2-1.6 \text{ nm/cm}^2\text{-year}$   
(with  $\beta = 6$ , Ba flux =  $7-10$  " )

$\text{CaCO}_3$  ( $30 \pm 5 \text{ umole Ca/cm}^2\text{-year}$ );  
ratio of Ba/Ca in forams -  $3 \times 10^{-6}$ :  
Carbonate carrier flux =  $0.1 \text{ nmole Ba/cm}^2\text{-yr.}$

Opal ( $45 \text{ umole Si/cm}^2\text{-year}$ );  
ratio of Ba/Si in diatoms -  $1.5-5.0 \times 10^{-5}$ :  
Opal carrier flux =  $0.7-2.3 \text{ nmole Ba/cm}^2\text{-yr}$

Acantharia ( $\text{SrSO}_4$  -  $220 \text{ nmole Sr/cm}^2\text{-yr.}$ , Brass, 1980);  
ratio of Ba/Sr -  $7 \times 10^{-3}$  (probably high, Arrhenius, 1963):  
Celestite carrier flux  $\leq 1.5 \text{ nmole Ba/cm}^2\text{-year.}$

(continued)



closer examination.

The general correlation of dissolved Ba with Si in the oceans has pointed to its possible involvement in the uptake and regeneration of opal. However, several investigations have failed to directly identify sufficient Ba in biogenic Si phases to account for the ratio of  $7 \times 10^{-4}$  seen in the water column correlations (Martin and Knauer, 1973; Ng, 1975; Libicki, 1976; Dehairs et al., 1980). The data presented in this work further support this and demonstrate that a significant fraction of the Ba which is present in the particles does not co-vary with Si during leaching.

The Ba/Si ratio in the bulk and HCl-washed Antarctic diatom samples was  $1.5 \times 10^{-5}$  and  $0.2 \times 10^{-5}$ , respectively. Other ratios for diatoms which have been reported range up to  $5 \times 10^{-5}$ . These phases, coupled with the surface biogenic Si flux, fall short of providing the required particulate Ba flux by at least an order of magnitude.

The composition of Radiolaria, the other major producer of opal, has not been studied. To estimate the possible importance of these organisms, one can assume that they contribute to the total surface flux of Si to the same degree as they make up the sedimentary budget ( $\leq 5\%$ , Lisitsin, 1972). If this is the case, then in order to account for more than 10% to the required Ba flux, Radiolaria must possess a Ba/Si ratio  $\geq 2 \times 10^{-3}$ . Determination of Ba in various washed-sediment Radiolaria samples demonstrated a ratio of only  $3-8 \times 10^{-6}$ , and there exists no other evidence to suggest that radiolaria could be so highly enriched in Ba.

Acantharia have been suggested as possible carriers by Brass(1980) but using his Sr flux estimates and the old Ba/Sr ratio reported by Arrhenius(1963) still yields a very small contribution to the Ba flux.

It has been shown for Ba and  $^{226}\text{Ra}$  (Edmond,1970; Chan et al.,1976) that the deep enrichment of these elements, which is seen to persist in the Antarctic, is inconsistent with their sole incorporation in a carbonate carrier. Examination of the biogenic  $\text{CaCO}_3$  phases in this study and in the literature (Thompson and Bowen, 1968; Boyle,1980) clearly demonstrates that they do not serve to transport significant Ba from the surface ocean.

Finally, the bulk plankton ratio of Ba/P, when coupled with the P-flux, also falls short of the required Ba flux - even when the ratio is modified by a regenerative enrichment of 6 ( $\beta$ ). Strong organic complexes with Ba are very unlikely in the presence of nearly any other divalent cation (Hughes,1972), however, simple ion exchange of cations frequently favors this weakly-hydrated element. Some fraction of the total Ba in the surface particulate matter may be bound by ion exchange similar to that for Ca and Sr (Bishop et al,1977). However, another major carrier phase or a dramatic change in the surface properties of the particles is required to carry enough Ba to the deep ocean.

Particulate barite ( $\text{BaSO}_4$ ) has been identified in suspended material (Chesselet et al.,1976), even though the ambient water column is clearly undersaturated with respect to that phase (Church and Wolgemuth, 1972). A more detailed analysis of GEOSECS-Niskin filter samples (Dehairs et al.,1980) have identified the systematic distribution of barite in several Atlantic profiles, with a distinct

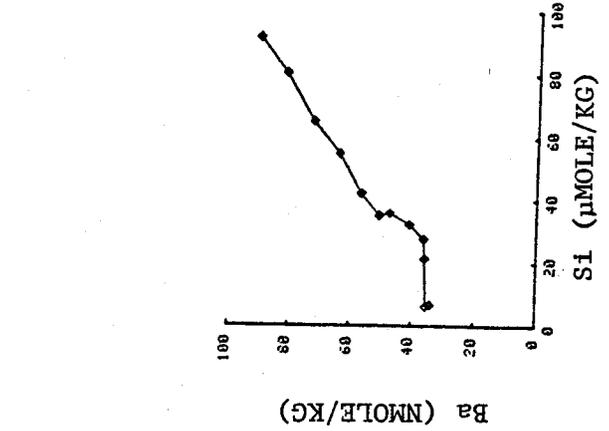
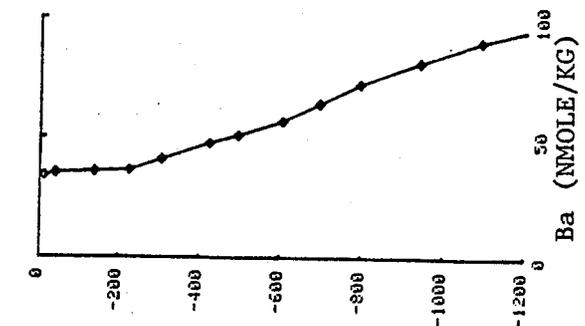
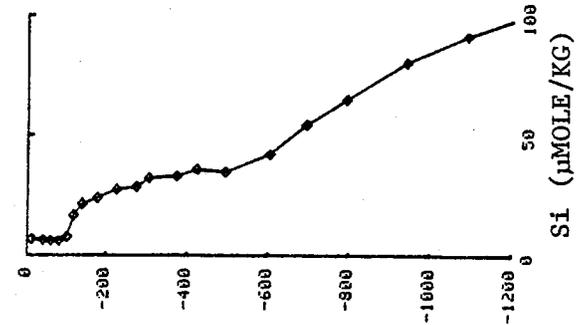
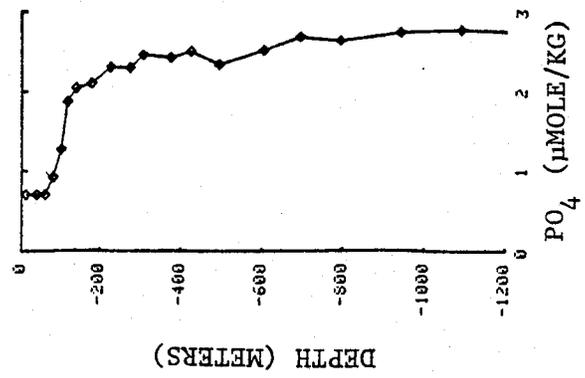
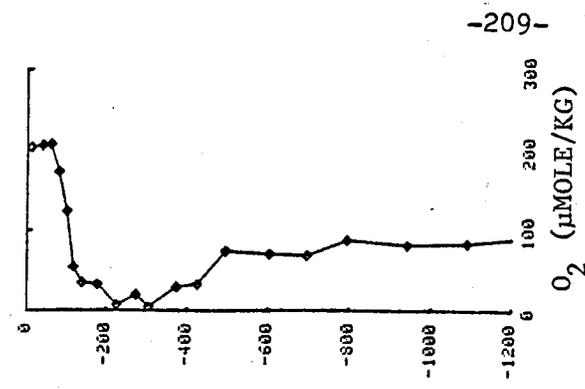
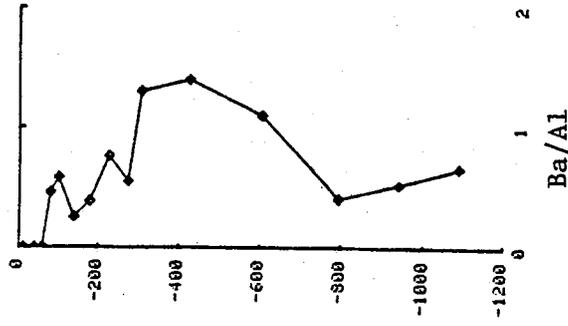
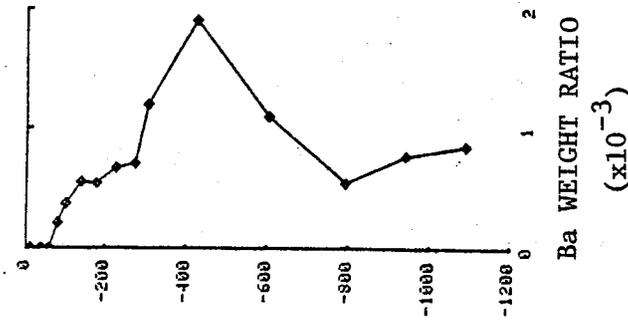
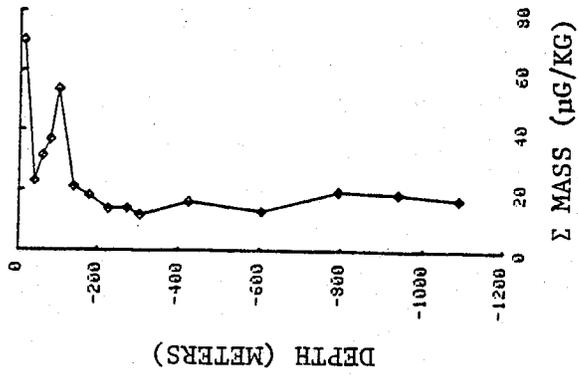
maximum coincident with the nutrient and oxygen extrema. From an inventory of these particles and application of settling models, these authors predicted a total flux of  $3.4 \text{ nmole Ba/cm}^2\text{-year}$  from the upper Atlantic. Of this, it is predicted that approximately one-half dissolves within the deep water column. This barite flux is still far short of being able to account for the deep Pacific enrichment. The Pacific barite data of Dehairs et al.(1980) are limited and show no systematic distribution.

The Pacific GEOSECS particulate data, collected and analyzed at Woods Hole (Brewer and Spencer, unpublished), and neutron activation analyses of the LVFS profile at the Galapagos site (Collier, unpublished) demonstrate a remarkable enrichment in particulate Ba with depth. This is much larger than, but similar in form to that seen in the Atlantic (Dehairs et al.,1980). The maximum occurs within the strong oxygen minimum present in the intermediate waters of the eastern equatorial Pacific. The particulate and dissolved Ba data along with other hydrographic properties at GEOSECS stations 331 and 337 are shown in Fig. IV-7. It is immediately clear that Ba is not removed from surface waters in a manner which is parallel to any of the "bio-limiting" nutrients. In fact, at station 331, the dissolved Ba concentration is nearly constant from 200 meters, up to the surface, while the nutricline is well developed by 100 meters. This distinct difference in the surface uptake-deep regeneration of Ba and Si is clearly seen in the pronounced "hook" in the near-surface dissolved Ba-Si plot. The striking features of the particulate data are the near-absence of Ba in the mixed layer and its dramatic increase in the upper

Figure IV-7. Particulate and dissolved Ba systematics at  
GEOSECS stations 331 (A) and 337 (B).

Particulate Ba data - Brewer and Spencer, unpublished.  
Dissolved Ba data - Edmond, unpublished.

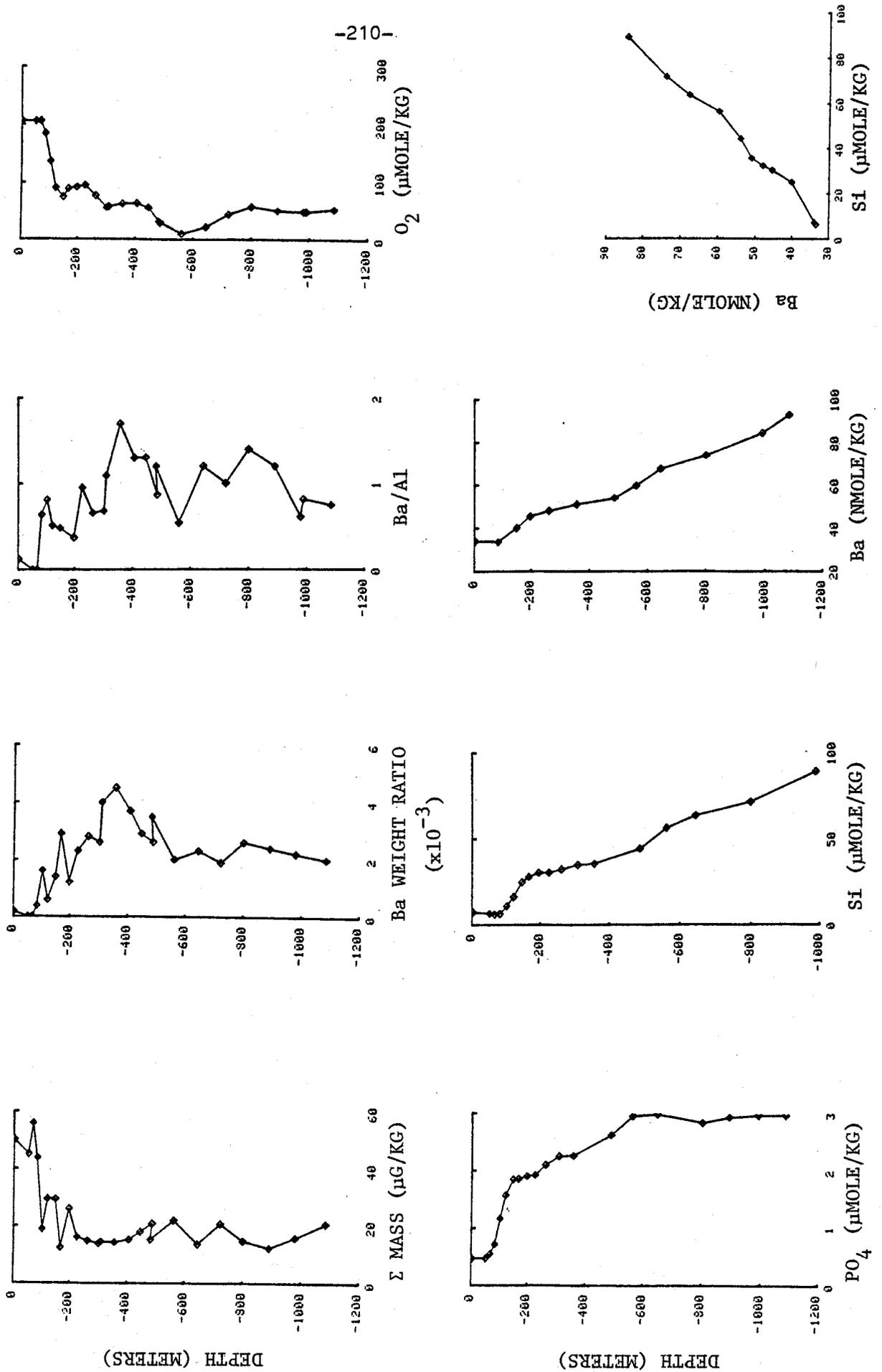
A



DEPTH (METERS)

DEPTH (METERS)

B



thermocline. There is not sufficient Ba in the surface material to create this Ba enrichment simply by the loss of other regenerated components. This can be checked by normalizing Ba to Al, which, assuming a steady state input, should be conservative through this settling process. The Ba/Al ratio still displays the same distinct maximum - demonstrating that the Ba must be derived in-situ.

In the LVFS profile, the concentration of Ba in the  $>53 \mu\text{m}$  particles increases from  $0.6 \times 10^{-3}$  (weight ratio) at 100 meters, to over  $3 \times 10^{-3}$  at 200 meters and  $4 \times 10^{-3}$  at 500 meters. These are consistent with the relative compositions of the GEOSECS particles shown in Fig. IV-7. At 500 meters in the LVFS profile, the estimated mass flux of Ba, based on size distribution-settling models, is  $40 (+10) \text{ nmole/cm}^2\text{-year}$ . Clearly this becomes an important flux of Ba with respect to the deep water enrichment and, if significant over larger areas, may be responsible for the particulate Ba flux anomaly.

The carrier phase, or description of the Ba association in these specific samples, has still not been documented but the similarity in form to the Atlantic barite profiles is suggestive of a similar process. Bishop et al.(1977) documented an increase in cation exchange capacity of the  $1-53 \mu\text{m}$  size fraction LVFS particles with increasing depth in the equatorial Atlantic. This change in the surface properties of the settling organic matter, coupled with the increase of dissolved Ba in the thermocline could provide a mechanism for the "uptake" of Ba, possibly followed by the precipitation of barite within decomposing organic aggregates. It is still possible that there exists some other organism responsible for the specific uptake of Ba in the upper

thermocline, although the possibilities have become quite limited. Only the direct and systematic examination of the particles involved can positively identify its carrier.

There is evidence of Ba regeneration in both the deep water column and the sediments. If the carrier phase is barite then it was originally formed out of equilibrium with the surrounding seawater. Subsequent exposure of the barite, possibly through the oxidation of protective organic coatings, will allow dissolution to begin. Dehairs et al(1980) noted barite grains from deep samples which displayed significant signs of dissolution.

Independent estimates from the fluxes measured in traps and the sediment are varied. The site S flux, collected by Dymond and Soutar (pers. commun.), is higher than that predicted by using the surface plankton carrier ratios - demonstrating the necessity of a secondary enrichment process occurring below the surface. The trap flux is also higher than the sediment accumulation rate, indicating the likelihood of bottom regeneration at this site. The sediment traps of Cobler and Dymond(1980) collected about 50 nmole Ba/cm<sup>2</sup>-year at the Galapagos site which is comparable to the high flux predicted from the 500 meter-LVFS sample. However, the documented input of hydrothermal Ba near these traps (Edmond et al., 1979a) may also contribute to the large Ba accumulation in the traps and sediments. It is difficult to distinguish between the surface and hydrothermally-derived flux at this point.

A pore water profile of Ba was reported by Church and Wolgemuth(1972) from a core taken in the vicinity of GEOSECS 337. It

shows a gradient of Ba, implying a flux into the bottom water. The coarse sampling interval (30 cm) would obscure any sharp concentration gradients which might have been present and similar to those seen for Cu in the upper 3 cm of other cores. Therefore, the estimated flux, approximately  $1 \text{ nmole Ba/cm}^2\text{-year}$ , represents only a minimum value.

The regeneration fluxes predicted within the linear T-S sections of the deep water column by the advection-diffusion models range from 4 to  $11 \text{ nmole Ba/cm}^2\text{-year}$ . The maximum value is at site 331 and, in a manner similar to Cu, the increased regeneration here could be related to the increased flux of settling particles which, in the case of Ba, are slowly dissolving.

### Iron

The geochemical cycle of Fe is not outlined in Table IV-15 because almost no good data exists on its distribution or primary inputs. Analytically, one of the most difficult elements due to contamination, it also has a complicated redox-chemistry, organic chemical functions, and colloidal properties. All of these factors have worked together to obscure the validity or systematics of any data or models on the marine distribution of Fe.

The plankton leaching experiment can be used to constrain at least one portion of the cycle. These experiments suggest that no regeneration of Fe along with any detected carrier phase is likely to occur in the water column. The total organic flux carrier-model predicts an Fe flux which is equivalent to the estimated surface input fluxes. This is consistent with a very short residence time and a

Table IV-15. Iron Cycle

- Primary input fluxes -

Rivers-  $C_r = ?$  (Boyle et al., 1977 - estimate  
for Amazon  $Fe \leq 1 \text{ nmole/cm}^3$ )

$$V_r C_r \leq 13 \text{ nmole Fe/cm}^2 \text{-year.}$$

Atmospheric-  $A = 50-60 \text{ nmole/cm}^2 \text{-year}$  (Wallace et al., 1977)  
(1% soluble)

Hydrothermal- maximum estimate based on  $^{21}\text{N}$  data -

$$V_h C_h \leq 70 \text{ nmole/cm}^2 \text{-year (K. VonDamm, unpublished)}$$

- Distribution of dissolved Fe - ??

- Box model for surface particulate flux:

$$P_{Fe} = (350 \text{ cm/yr}) \times (\Delta \text{ conc.}) + (50 \text{ to } 150 \text{ nmole Fe/cm}^2 \text{-year})$$

- Independent estimates:

Using carrier flux ratios -

Total organic matter flux as P ( $0.87 \text{ } \mu\text{mole P/cm}^2 \text{-year}$ );  
plankton Fe/P ratios -  $5-15 \times 10^{-3}$ ;  
Fe flux =  $4-13 \text{ nmole Fe/cm}^2 \text{-year}$ .

distribution that is probably similar to that of Mn. The rapid scavenging should allow significant variations in the local particle flux because of the heterogeneity of the primarily-atmospheric input flux. This heterogeneity is reflected in the variability of Fe/P in the surface plankton samples.

### Vanadium

A particulate profile of V was presented in Fig. IV-1. The V was rapidly regenerated from the particles as demonstrated by the decrease in the V/Al ratio. Throughout the upper profile the V/P ratio in the particles was a constant  $- 4 \times 10^{-3}$ . A total flux of P to the deep ocean of  $0.87 \mu\text{mole/cm}^2/\text{year}$  would result in a corresponding V flux of  $3.5 \text{ nmole/cm}^2\text{-year}$ . Systematic determinations of dissolved V in seawater are lacking, but reported values range between 30 and 50 nmole/kg (Brewer, 1975). The river input is also poorly known, but it is probably  $\leq 0.1 \text{ nmole V/cm}^2\text{-year}$  (Martin and Maybeck, 1979). Assuming that the particulate V flux can be represented by the V/P ratio and the P flux, a deep water-surface water enrichment ( $C_d - C_s$ ) of 9.6 nmole V/kg is calculated. If this surface uptake and flux of V is a general feature in other marine environments then a surface depletion of V, on the order of 10 nmole/kg, should exist. This is a case where the carrier model has been used to predict an unknown water column distribution.

Summary of biogenic trace element fluxes.

Table IV-15 presents the average element/P ratios in the surface plankton and the flux estimates using the total organic carrier model. These can be used as the starting point for future studies of regeneration processes using shallow and deep sediment traps. The predicted values of  $\beta$  are used to give the ratios that should be seen in the shallow traps. To monitor deep releases of the trace elements, as regenerative processes further fractionate the particulate material, it is useful to normalize the trace elements to other components which are more refractory than the P, such as organic carbon,  $\text{CaCO}_3$ , opal, and clay. This technique was used in the normalization of Ba and V to Al in vertical profiles of suspended material to identify their uptake and regeneration with respect to a refractory particulate component.

Table IV-16. Summary of organic (P) carrier ratios and estimated surface fluxes.

Element	Me/P measured ( $\times 10^{-3}$ )	factor $\times$ enriched { $\beta$ }	Me/P settling ( $\times 10^{-3}$ )	Surface flux estimate ( $\text{nmole}/\text{cm}^2\text{-year}$ )	
				P carrier	box model (dissolved distribution)
P					870
Cd	0.6	0.7	0.4	0.35	0.34
Ni	0.8	2.4	2	1.7	2.7
Mn	0.4	2	0.8	0.7	2.2
Cu	.54	3.4	1.8	1.6	1.3
Zn	4	6	20	17	2.4
Ba	1.5	6	9	8	37
Fe	10	6	60	50	
V	4	(1)	4	3.5	

Chapter V

Conclusions

V. CONCLUSIONS - MARINE BIOGEOCHEMISTRY OF TRACE ELEMENTS.

Surface plankton samples have been carefully collected and analyzed for major and trace element composition. The experiments performed on these samples have clearly demonstrated the significance of biogenic particulate phases in determining the fluxes of trace elements out of the surface ocean. A carrier model was successfully used to estimate these fluxes in proportion to the major nutrient element cycles.

Terrigenous Carriers

The refractory behavior and element ratios of Al and Fe demonstrated the presence of an aluminosilicate phase within the plankton samples. This was present in all samples - even from the more remote regions of the central equatorial Pacific and Antarctic. In no case did this refractory phase contribute significantly to the other trace elements in the samples. The flux estimate for terrigenous Al carried within the biogenic samples ranged between 0.005 and 0.1  $\mu\text{mole Al/cm}^2\text{-year}$ , based on the range of compositions detected. This variation is a function of the input flux of terrigenous materials and of the biological production rate at the sampling site.

A trace level of Al was detected that was directly associated with the biogenic material. This was identified by its solubility in dilute HCl and probably was derived from dissolved Al in the surface water. The flux of this phase is estimated to be on the order of 1 nmole  $\text{Al/cm}^2\text{-year}$  - only a small fraction of the estimated river input of

dissolved Al. To quantify the complete geochemical cycle of Al, particulate trace element studies need to determine the chemical nature of the total particulate Al before it is simply assigned to silicate phases.

#### Biogenic Carriers

The primary carrier for all other elements studied was the non-skeletal organic fraction of the particulate material. Direct examination of  $\text{CaCO}_3$  and opal demonstrated that these phases contained only small percentages of the trace elements in the plankton.

The organic associations included an extremely labile fraction containing P, Cd, Ni, and Mn which was rapidly released into sea water and distilled water. Cell lysis, active excretion, and bacterial decomposition were noted as effecting this rapid release of 40 to 60% of the initial concentration of these elements. The box models for these elements suggest that this recycling must occur very near to, or within the surface reservoir and results in a change in the ratio of metal/P in the settling particles. Near-surface sediment trap experiments and suspended particulate sampling should detect this process. The ratio of Ni and Cu to P should increase by a factor of 2-4 and the Cd/P ratio should be only 60-90% of the ratio determined in the fresh surface plankton. Since bacterial activity and osmotic shock have been identified as variables in this process, special care must be taken to determine the effects of trap poisoning and the loss of cell fluids during collection or storage.

The other major fraction of the trace elements in the plankton samples was more strongly bound to fixed organic sites. The regeneration of this fraction appears to be more metal-specific and related to the stability of the organic complexes involved. The particulate-Cu complexes are stable in the water column but decompose rapidly at the sediment interface, releasing the metal, while the Ni complexes in this fraction begin to decompose well above 1500 meters in the water column. The nature of these specific metal-organic complexes needs to be investigated. Identification of the nature and chemistry of the organic Cu-complexes in surface sediments should be possible. Henrichs(1980) has demonstrated that the composition of the dissolved free amino acids in surface sediments reflects the in-situ activity of bacterial metabolisms. This activity is sufficient to dominate any signal from the original planktonic input and probably reflects the process which destroys the Cu carrier.

Although the metal-organic biochemistry is still poorly characterized, the carrier relationships can be used to quantify trace element fluxes and identify major processes affecting their distribution.

Relationships between the dissolved and particulate composition of surface waters.

Systematic variations in the surface water concentrations of nutrients and trace elements have been noted (Boyle et al.,1975; Bruland,1980; Boyle et al.,1980). Plankton samples taken from the Antarctic upwelling regions demonstrated a decrease in their total

trace element concentrations as the dissolved concentration of nutrients and trace elements increased. These observations led to a closer examination of these relationships in the Pacific samples.

The concentrations of the non-terrigenous trace elements were relatively constant in the plankton, when normalized to P, as compared to the same ratios in surface water. These particulate compositions are primarily determined and limited by the properties of the organic materials and metabolism of the plankton and do not appear to respond directly to the dissolved concentrations in the surface water. This emphasizes the importance of specific metal-organic complexes as carriers.

Variations in the dissolved concentrations of surface waters as a function of the production of the biogenic material were also noted. The concentrations of Zn and Cd are depleted to very low levels in surface waters along with P. The ratios of these metals to P in the plankton samples, are always greater than, or equal to the surface water values. In the case of Cd, this may be responsible for its depletion before that of P as upwelled waters evolve into normal surface waters. The concentrations of Cu and Ni in surface waters do not approach zero. The formation of the biogenic material, which possesses a relatively constant metal/P ratio that is lower than the upwelled water, becomes limited by the depletion of the nutrients.

### Geochemical cycles

The trace element-major element ratios determined in the plankton samples and their regeneration products have provided a basis for outlining the marine geochemical cycles of these elements. A simple, two-reservoir box model has been used to predict the average flux of each element via biogenic material.

Several specific experiments need to be pursued in support of the predictions made by the carrier models. There are differences between the ratios of Cd, Cu, and Ni to P measured in surface plankton compared to those predicted by the carrier-box model. These have been interpreted as evidence of rapid cyclic regeneration of the organic material within the surface ocean which results in changes in the element/P ratios in the residual settling material. These changes should be measurable in carefully-collected suspended and settling particles.

The depletion of Cd and P in the eastern North Pacific suggests that there must be a significantly lower Cd/P ratio in plankton sampled from surface waters in transition zones into oligotrophic environments. Again, a series of plankton and water samples across such a region is needed.

The co-variation of V with P in a suspended particulate profile has been used with the carrier model to predict a surface water V depletion of approximately 10 nmole/kg over its deep-water concentration. The dissolved distribution of V in sea water is unknown but its concentration is estimated to be approximately 40 nmole/kg. To test the predicted surface depletion, an analytical method must still

be perfected and systematically applied to the determination of several vertical profiles of V.

The production of a sub-surface Ba carrier, such as barite, is necessary to balance the magnitude of that element's deep enrichment. The eastern equatorial Pacific displays a dramatic increase in particulate Ba within the upper thermocline and should be the best place to study this process which may be related to the high surface productivity coupled with the intense oxygen depletion of the sub-surface waters.

The average fluxes estimated by the carrier-box model must now be supported by direct suspended-matter and sediment-trap measurements in the near-surface and deep ocean. The flux of biogenic material to sediment traps is directly dependent on the magnitude of the total surface productivity. This varies by more than a factor of ten between different surface-ocean environments. Until many more trap experiments can quantify these variations, available results must still be extrapolated using carrier models to describe the total fluxes of trace elements to the deep ocean and sediments.

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APPENDIX I. SUMMARY OF HYDROGRAPHY, PLANKTON TOWS, AND  
SEDIMENTS FROM SAMPLING SITES.

Antarctic Samples

Plankton tows and surface water samples were collected from Atlantis II, cruise 93-IV, during January, 1976 along a line between Capetown, South Africa, and the Antarctic circle at  $30^{\circ}\text{E}$  (Fig. A I-1). This section crosses the Antarctic circumpolar current, a region of active upwelling with high rates of primary production dominated by diatoms. The three tows analyzed are from stations E( $48^{\circ}\text{S}$ ), J1( $60^{\circ}\text{S}$ ), and M( $67^{\circ}\text{S}$ ).

The surface water properties of the circumpolar current are primarily determined by the progressive outcropping of denser isopycnals as one moves toward the southern divergence region between the west wind drift and the westward moving coastal currents (Gordon, 1971). The northward Ekman component of this eastward flow sinks below the warmer Subantarctic surface water creating a sharp frontal system known as the Antarctic Convergence. This is a region of extreme horizontal water property gradients and associated ecological barriers. The more northerly Subantarctic surface water is itself a complicated mixture of warmer subtropical waters and upwelled antarctic intermediate waters. The frontal system where this water mass meets the northern subtropical surface water is the Subtropical Convergence.

The surface water nutrients from the AA transect are plotted in Fig. A I-2 along with the same properties from a vertical profile at GEOSECS station 66 in the southern Argentine Basin. In general, the variation of  $\text{PO}_4$  and Si with respect to temperature in the surface

Figure A I-1. Antarctic sample locations and surface temperature distribution.

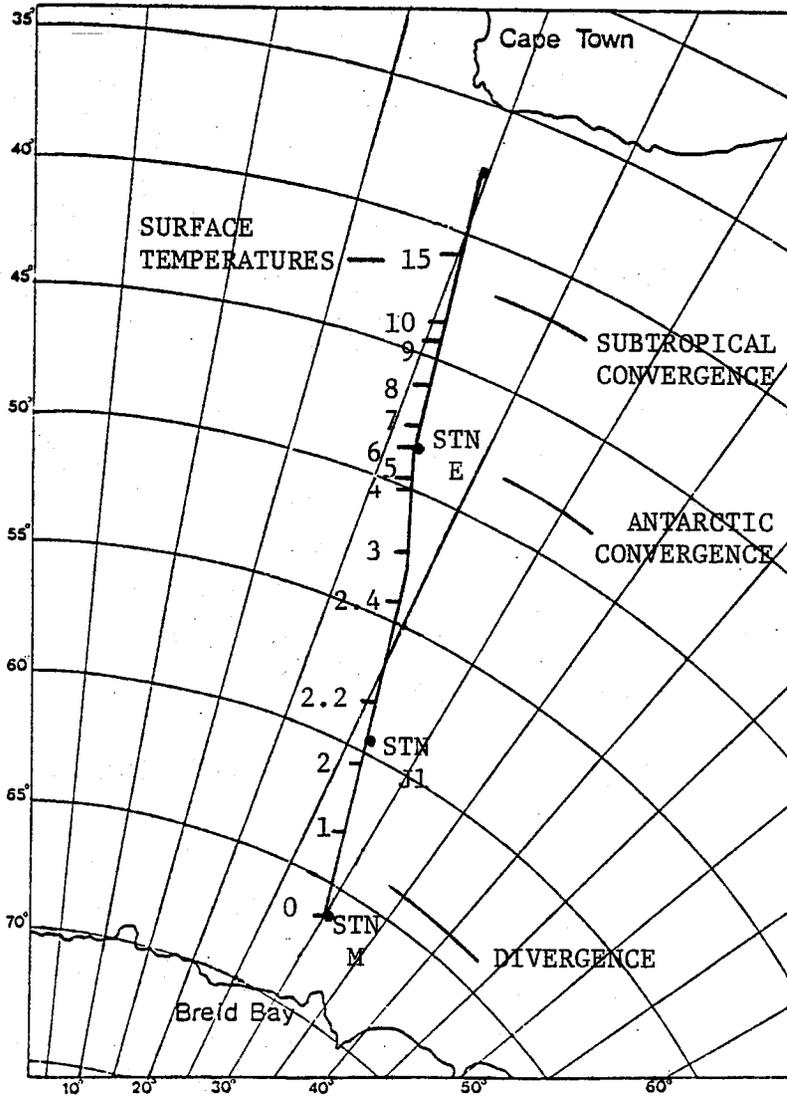
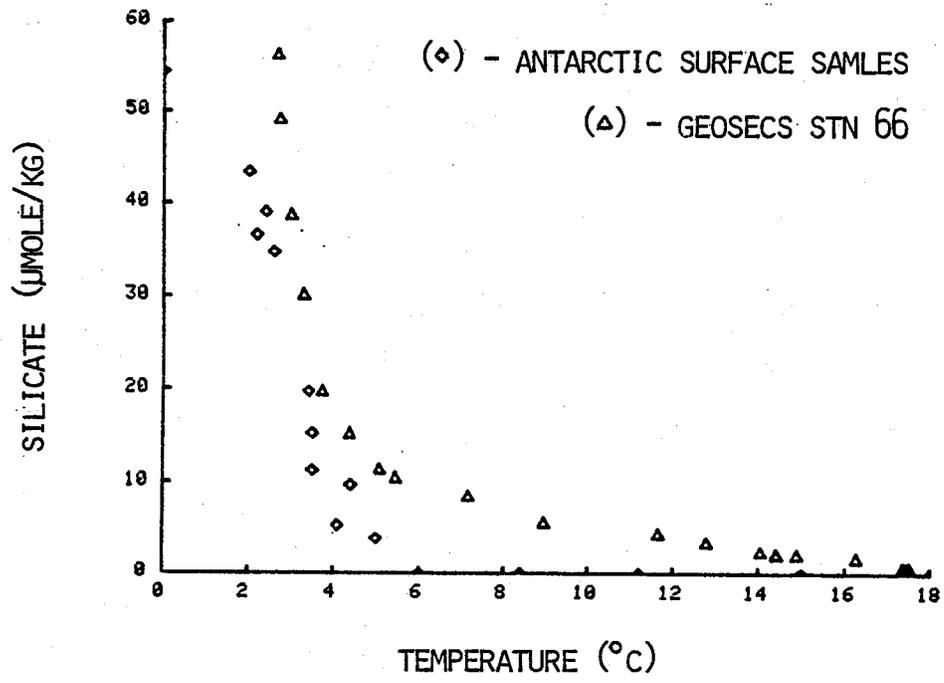
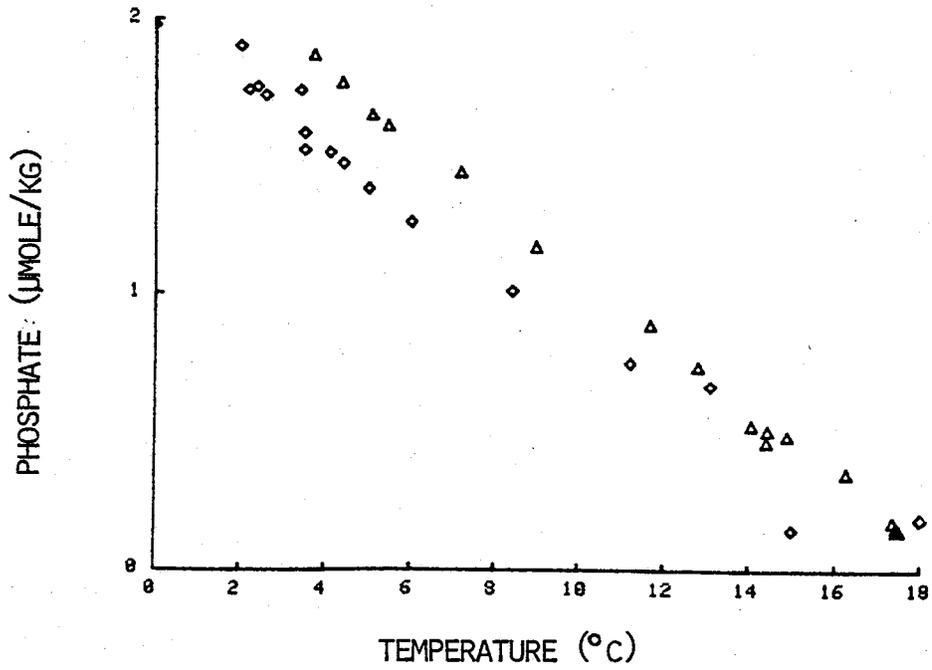


Figure A I-2. Antarctic surface  $PO_4$  and Si vs. temperature.

A



B



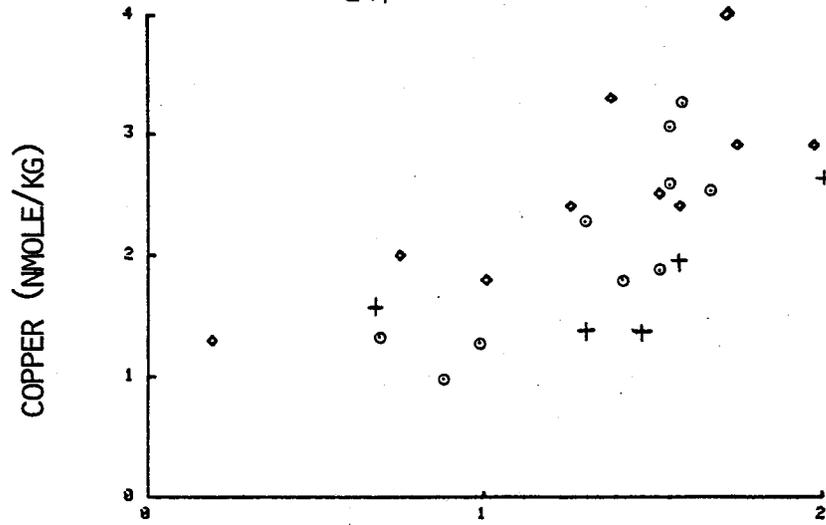
waters follows the same distributions as the vertical profile. This shows the dominance of upwelling in determining the surface water composition. The concentrations of  $PO_4$  and Si are often somewhat lower than those at the same temperature in the profiles reflecting biological uptake in older surface waters and possibly a component of cooled surface water remnant from the winter season.

The concentrations of Cu, Ni, and Cd all increase in the upwelled water and are plotted against  $PO_4$  in Fig. A I-3. Similar behavior has been reported on a transect of the Antarctic circumpolar current south of New Zealand (Boyle and Edmond, 1975; Sclater et al, 1976) and these data are also plotted for comparison. Vertical profiles of these trace elements were determined at GEOSECS 293 in the southwest Pacific by Boyle (1976), and these data are plotted in Fig. A I-3. Again, the nutrient-trace element relationships in the surface transect parallel those in profile north of the upwelling zone. The variation of Cu with respect to  $PO_4$  (Fig. A I-3) is generally equivalent to the New Zealand data but the slope of the regression is 30-40% lower and it does not pass through the origin. The concentration of Ni also increases with "depth" along this inverted profile (Fig. A I-3). The relationship with  $PO_4$  is somewhat different than that of Sclater et al (1976) and there is no improvement in a multiple linear regression using both  $PO_4$  and Si to describe the shallow and deep regenerative behavior. Cadmium and  $PO_4$  display the now-familiar covariance with a slope of  $3.3 \times 10^{-4}$  (absolute mole ratio) which is comparable to the vertical profile slope of  $3.5 \times 10^{-4}$  (Boyle et al, 1976; Bruland, 1980). If the deviation of the surface  $PO_4$  distribution from that of the profiles (Fig. A I-2)

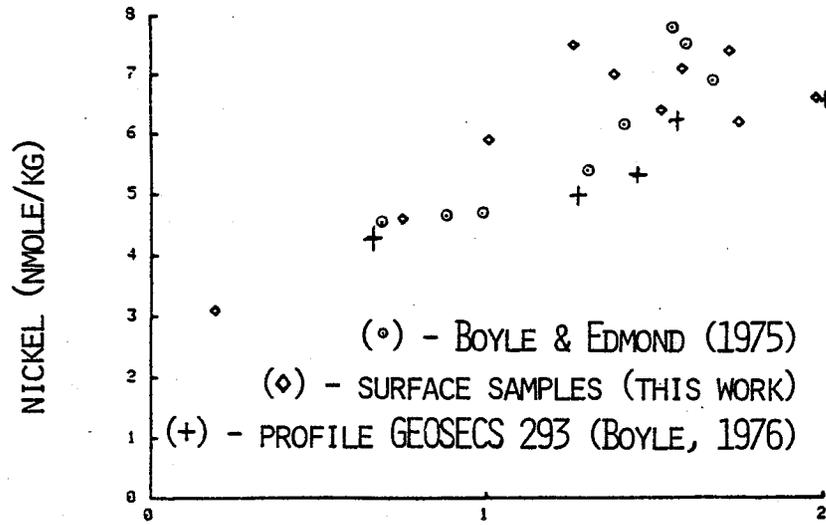
Figure A I-3. Antarctic surface Cu, Ni, Cd vs.  $PO_4$ .

Line on Cd-P figure indicates deep Pacific regression with a Cd/P slope of  $0.35 \times 10^{-3}$  (Boyle et al., 1976; Bruland, 1980).

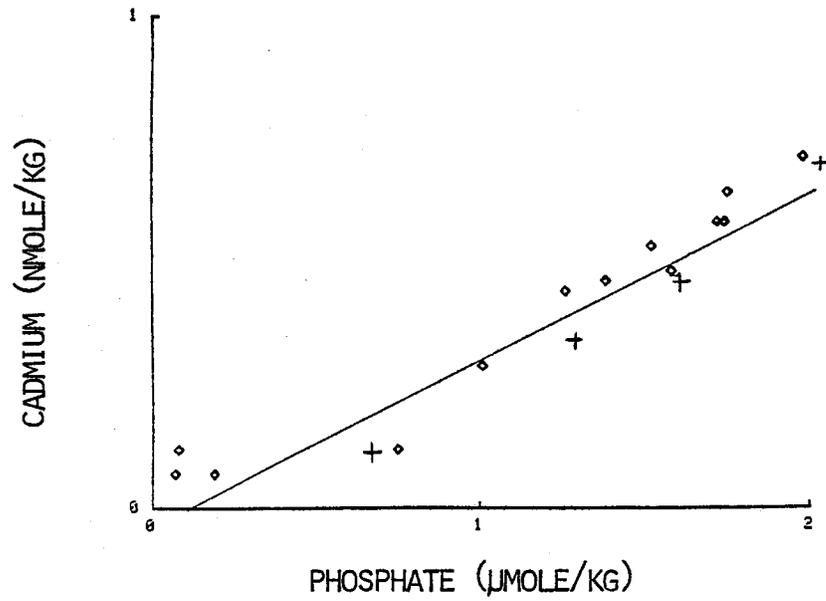
A



B



C



reflects removal of  $PO_4$  from the upwelled water by biological uptake then the maintenance of a constant  $Cd/PO_4$  ratio is support of Cd covariance with  $PO_4$  during the uptake process as well as regeneration.

The circumpolar upwelling region is one of the most productive areas in the world and accounts for the bulk of biogenic opal fixation in the oceans. Koblentz-Mishke et al(1970) estimate the average annual carbon fixation to range from 100 to 250 mg C/m<sup>2</sup>-day across this section but there are wide variations between summer and winter rates in this light limited environment. Using these figures and an average diatom Si/C mole ratio of 0.37, Lisitsin(1972) has estimated silica production to range from 250 g SiO<sub>2</sub>/m<sup>2</sup>/year near Africa to over 500 in the circumpolar current between the convergence and the divergence. The sediment distribution reflects the variations in surface productivity (Goodell et al,1973). Rising out of the Agulhas Basin, the sediments quickly grade from calcareous to siliceous ooze over only a few degrees of latitude which correspond to the mean location of the polar front. The siliceous ooze is more than 70% by weight opal in a belt between 50 and 63°S where it begins to grade towards the terrigenous deposits of the Antarctic continent. Demaster(1979) has shown that these sediments are actively winnowed and redistributed by the strong circumpolar and slope currents.

All tows collected on this leg were consistent with this zonal pattern of productivity as the absolute mass of the surface suspensions increased (qualitatively) in the southward direction. Nearly all of the mass and numbers of individuals in the tows were diatoms (Table A I-1) and the species types and gradations were consistent with other

studies in this region (Steyaert, 1974). The most southerly station (M), which appeared to be on the south side of the divergence, yielded a large mass of plankton towed from numerous surface patches of organisms. The diatoms in this sample were very nearly a single species "bloom" (*Corethron* sp.), yet did not appear to be in healthy condition based on their low organic carbon (Demaster, personal comm.) and phosphorus content.

#### Eastern Equatorial Pacific Samples

A station in the Equatorial Pacific, east of the Galapagos Islands ( $0^{\circ} 45' N$ ,  $86^{\circ} 10' W$ ; Fig. A I-4) was occupied on two separate occasions in association with research activities on hydrothermal processes at the Galapagos rift system. In June-July, 1976, a vertical profile of suspended particulate material was collected by large volume, in-situ filtration (LVFS) from the R/V Melville during leg II of the Pleiades Expedition. Plankton tows were attempted from a Zodiac but failed due to technical problems coupled with low levels of productivity present at the time of sampling. In March, 1977, the site was reoccupied by the R/V Knorr, cruise 64-02, during the first ALVIN diving program on the ridge axis. Three plankton tows were collected by hand from a Zodiac and processed at sea.

The eastern Equatorial Pacific is a region of high productivity due to upwelling under the equatorial divergence. This extreme eastern station also experiences a seasonal influx of cool, nutrient-rich water from the Peru-Ecuador coastal upwelling regions. The circulation of water masses in the region is extremely complicated and subject to

Table A I-1. Antarctic Samples - Description of Tows.

-Towed from a boom off the starboard bow of the R/V Atlantis II  
-Daytime tows at approximately 5 meters depth, 1.5 knots, 30 mins.

(plankton groups listed below each station by descending numbers of individuals (estimated))

STN E (47° 52'S, 22° 22'E) relatively small mass.

Rhisolenia sp.  
Chaetoceros sp.  
Coscinodiscineae

STN J1 (59° 49'S, 27° 07'E) medium density collected.

Nitzschia sp.  
Rhizosolenia sp.  
Corethron sp.  
Coscinodiscineae

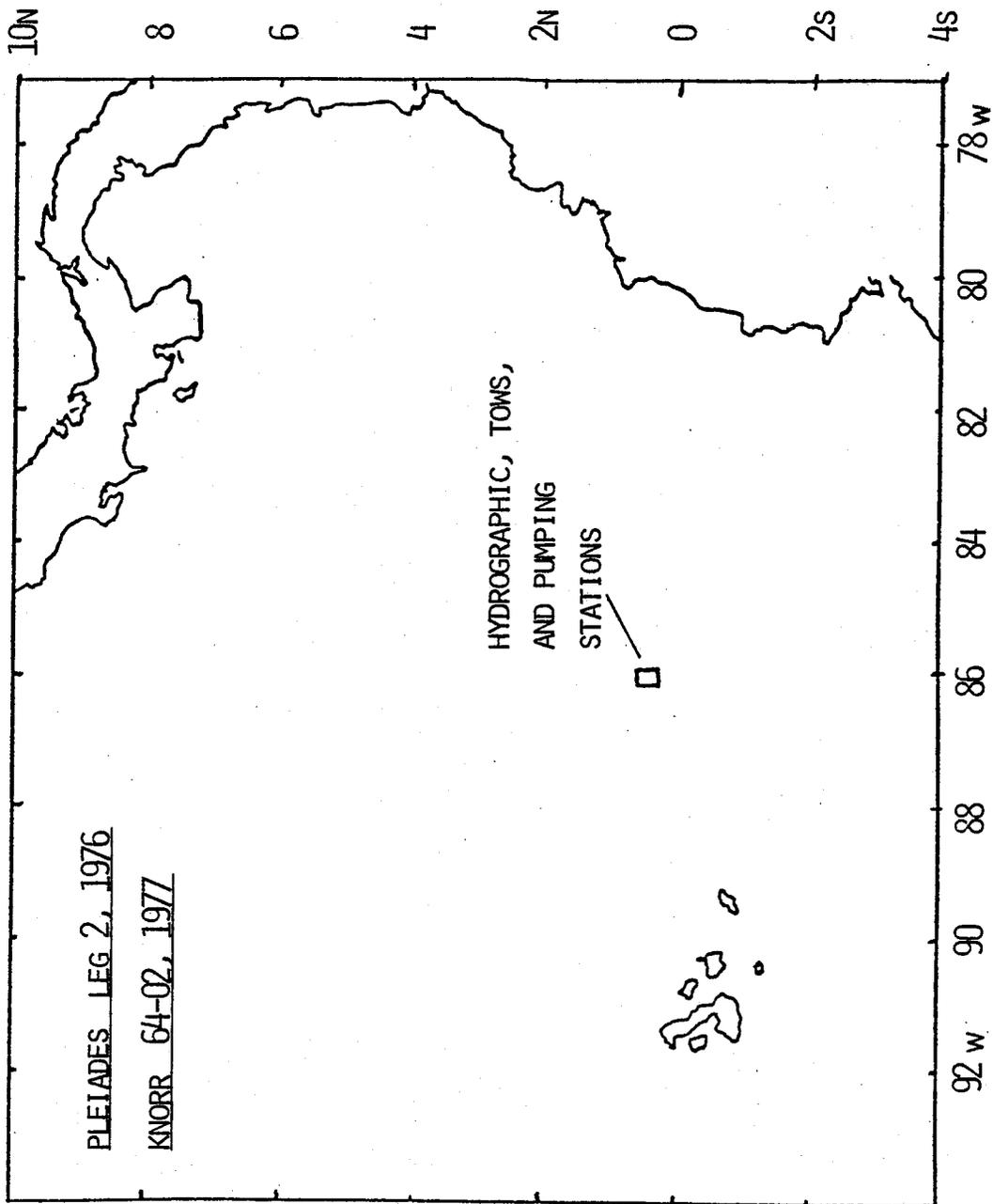
STN M (66° 44'S, 30° 00'E) very large mass collected.

Corethron sp. (greater than 99% of total number)  
Coscinodiscineae

Surface water properties:

STN	T	PO <sub>4</sub>	Si	Cu	Ni	Cd
E	6.0	1.26µM	<1µM	2.4nM	-	0.44nM
J1	2.4	1.75	39.1	2.9	6.2	0.64
M	0.0	1.98	54.4	2.9	6.6	0.71

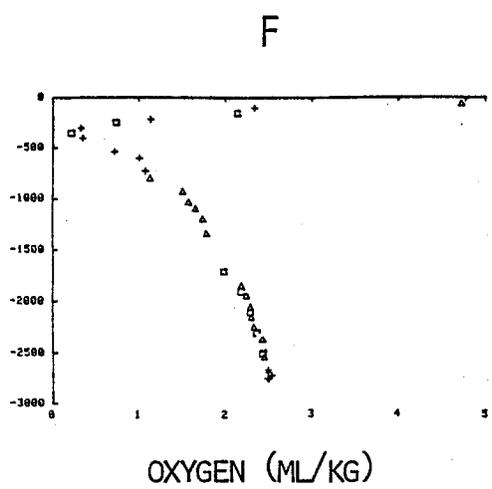
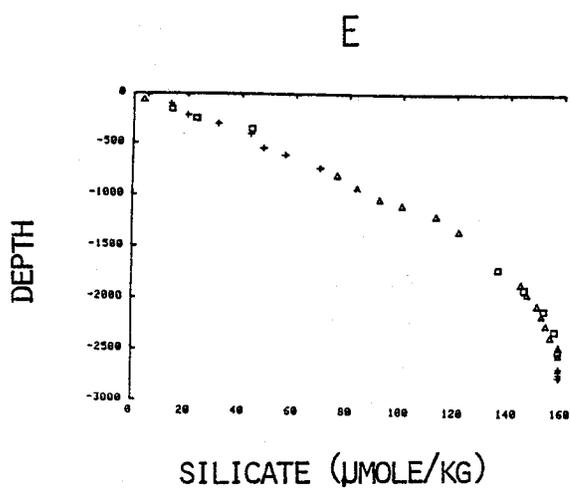
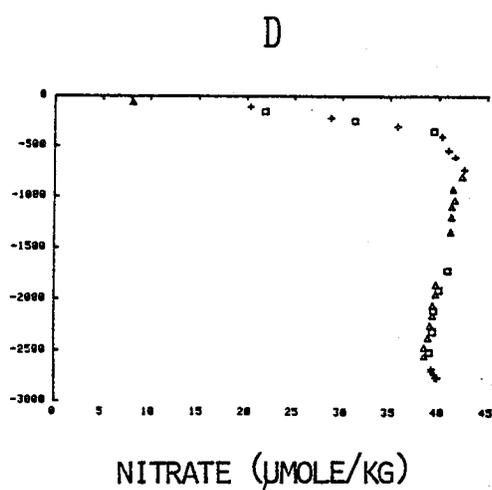
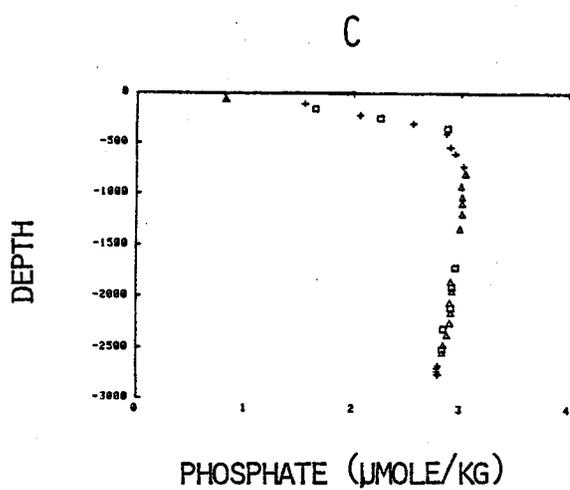
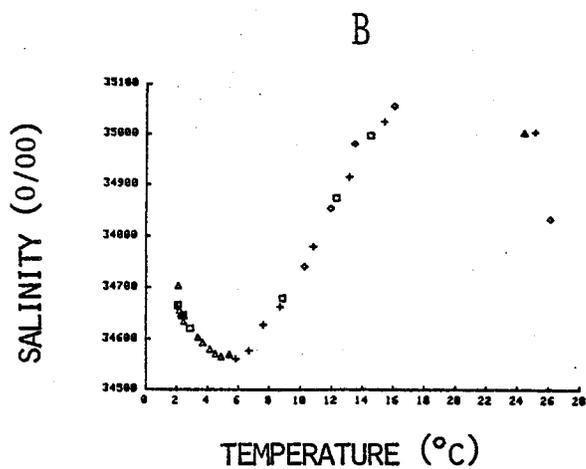
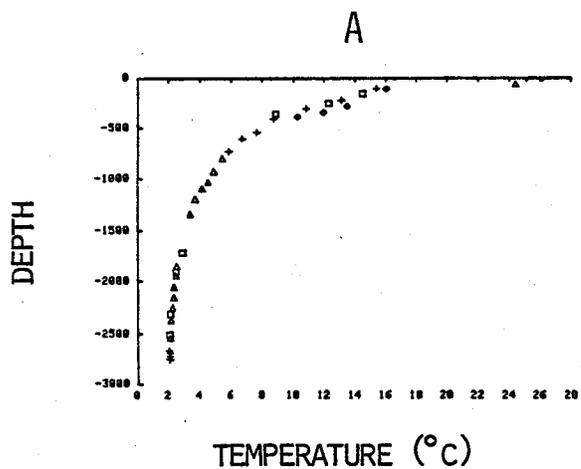
Figure A I-4. Galapagos sample locations.



seasonal and longer term variability connected with "el Nino" events (Wyrтки, 1967). The main feature at the sampling site is the north-south movement of the Equatorial Front separating the Tropical Surface Water(TSW) on the north from the Equatorial Surface Water(ESW) on the south. The TSW is warm, low-salinity, and nutrient poor. It supports a relatively low level of productivity. The properties of the ESW are determined by a complex and variable mixture of the upwelled Peru current waters, subtropical surface waters, and waters upwelled directly along the equator (Wyrтки,1966). The resulting water is higher in salinity and nutrients, and is colder than the northern water mass, sometimes by several degrees. This is the water mass that supports high levels of productivity in the region.

The hydrographic data for the Galapagos site are shown in Fig A I-5. The major differences between the two sampling dates is seen in the surface water where the temperature was lower and the nutrient concentrations were correspondingly higher in March, 1977. The profiles below the upper 200 meters were essentially identical. The nitrate and phosphate increase rapidly in a 15:1 ratio through the thermocline to a distinct discontinuity at the oxygen minimum (approx. 375m), from which they increase more slowly to their maximum values near the salinity minimum. Calculations of oxygen consumption rates based on decreases in particulate organic carbon fluxes at the time of the LVFS station (Bishop et al, 1980) show that the oxygen minimum cannot be created in-situ by vertical processes but must be a horizontal expression of high rates of regeneration below the coastal upwelling regions or of higher surface productivity events during other

Figure A I-5. Galapagos hydrographic data.



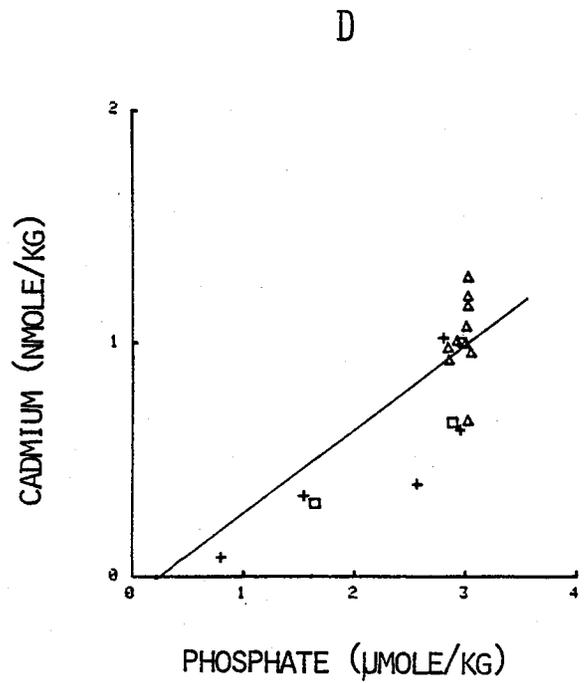
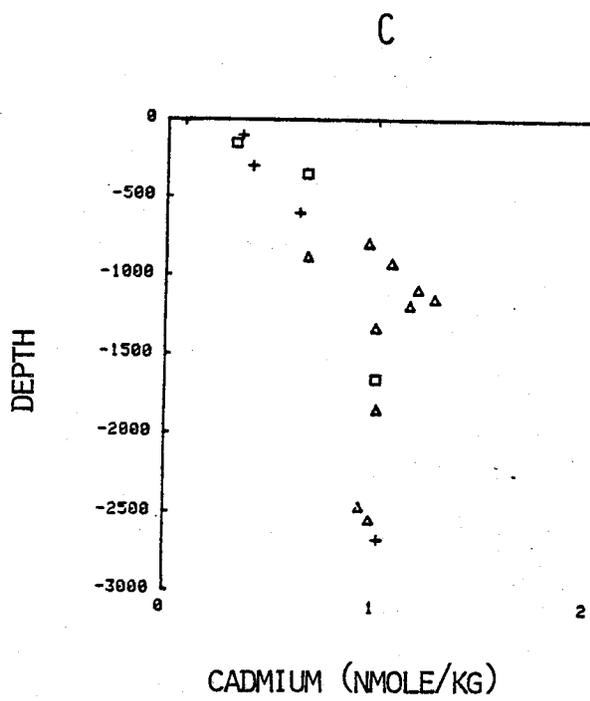
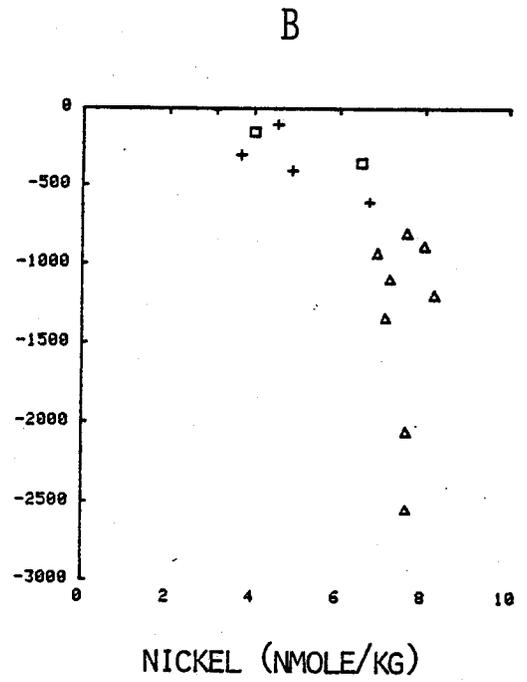
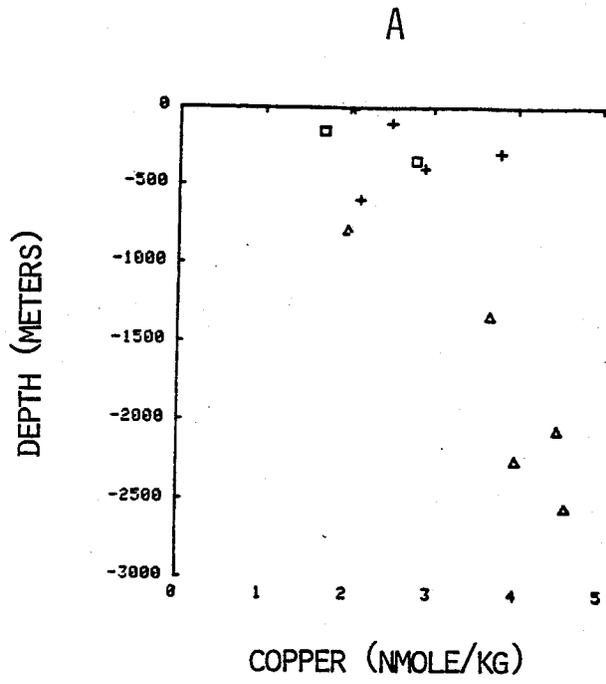
seasons.

The water column trace elements at this station were collected using a prototype in-situ syringe sampler which, due to technical problems, collected only a small volume of useable water and was prone to contamination and leakage. The vertical profiles of Cu, Ni, and Cd are plotted in Fig. A I-6 and the scatter in the data attest to the sampling difficulties. In general, the form of the depletion at the surface and regeneration at depth is similar to other Pacific stations. The Cd - PO<sub>4</sub> relationship shows a deviation from the linear slope of  $0.35 \times 10^{-3}$  seen in other Pacific profiles. Although the form of this deviation can be seen in the upper waters of all profiles, this is by far the most extreme case of this low Cd/P slope reported. It is possible that this is a function of the separation of the uptake or regenerative behavior of these two elements in this environment.

The major element chemistry, biology, and vertical flux of the particulates collected at the LVFS station have been discussed by Bishop et al(1980). The water column concentration and calculated flux of particulates were very low compared to mean productivity estimates (Moore et al,1973) and to measured sediment trap fluxes and sedimentation rates (5 cm/1000 yr, Cobler and Dymond,1980). Namias(1978) has shown that 1978 was a "Nino" year and the normal flux of Peru upwelling water was absent at this station. The net flux of organic carbon out of the 40 meter mixed layer was calculated to be 130 mg C/m<sup>2</sup>-day which can be taken as a minimum estimate of the productivity. This value can be compared to the Eastropac average of over 500 at this site (Moore et al,1973).

Figure A I-6. Galapagos dissolved Cu, Ni, Cd profiles.

Line on Cd-P figure indicates deep Pacific regression with a Cd/P slope of  $0.35 \times 10^{-3}$  (Boyle et al., 1976; Bruland, 1980).



The tows collected in 1977 had considerably more mass than those attempted in 1976. They contained a relatively greater proportion of Acantharia, Dinoflagellates, and invertebrates (Table A I-2) compared to collections on the LVFS filters. No direct comparison has been made between the two sampling systems. The Nitex materials in both the net and pump are similar in size (44 and 53 $\mu$ m) but the pump can be expected to be biased away from the more mobile invertebrates. Even so, every comparison of the two sampling programs shows a significant difference in the standing crop and species makeup of the biogenic material - the net tows collecting more of the mobile zooplankton.

The sediments of the eastern Equatorial Pacific reflect high levels of productivity with a thick band of carbonate and siliceous material running under the Equator (van Andel et al, 1975). Studies of the biogenous sediments under the Galapagos site have been published by Moore et al (1973). They have shown that the distribution and mass of biogenic sediments within the basin do not reflect the details of the surface productivity distribution, and were subject to resuspension, dissolution, and mixture with lithogenous components. In their analysis, which suggested significant amounts of bottom dissolution of  $\text{CaCO}_3$ , they assumed that the composition of biogenic suspended material delivered to the sediments was constant over the whole basin, was 95%  $\text{CaCO}_3$  (excluding organic matter), and had a  $\text{CaCO}_3/\text{SiO}_2$  weight ratio of 20. The LVFS material, the plankton tows, and the sediment trap material collected by Cobler and Dymond (1980) had  $\text{CaCO}_3/\text{SiO}_2$  ratios of 0.3, 2.5, and 2.5, respectively, indicating significantly more opal production and temporal variability of the ratio. Although these may

Table A I-2. Galapagos Samples - Description of Tows.

-Towed from inflatable Zodiac, upwind of R/V Melville.  
-Daytime tows, vertical hand winched, 5-30 meters depth.

TOW 1 - 3/14/77                    approx. 225ml wet volume collected.  
TOW 2 - 3/17/77                    100ml  
TOW 3 - 3/21/77                    250ml

All tows were similar in relative distribution of organisms and are summarized below in order of decreasing mass contribution.

- I. Diatoms - Rhizosolenia sp., Planktoniella sol, and a variety of discoid species.
- II. Copepoda - adult Calanus sp. and numerous nauplii.
- III. Acantharia - numerous and in good condition.
- IV. Dinoflagellates - Ceratium sp.
- V. Misc - Tintinnids and Pteropods

Surface water properties:

T	PO <sub>4</sub>	NO <sub>3</sub>	Si	Cu	Ni	Cd
26	0.80µM	8.0µM	5.2µM	2.06nM	2.99nM	0.08nM

represent anomalous conditions, the ratios are much closer to the measured surface sediment ratios (3-5), and the degree of carbonate dissolution predicted should be reassessed.

#### Central Pacific Samples

During May, 1979, two sets of tows were collected from the R/V Knorr (K79-05) during the MANOP surveys of site "C" ( $1^{\circ}\text{N} - 139^{\circ}\text{W}$ ) and site "S" ( $11^{\circ}\text{N} - 138^{\circ}\text{W}$ ) (Fig. A I-7). Site C is within the shallow, westward-flowing South Equatorial Current and underlain by the east-flowing Equatorial Undercurrent. The divergent flow of the surface current near the equator causes the upwelling of deeper, nutrient-rich water which is responsible for the band of high productivity through this region. At the time of sampling, site S was within the eastward-flowing Equatorial Countercurrent but during the fall-winter months the front between this current and the North Equatorial Current moves south of the station. The Countercurrent carries Tropical Surface Water which is warm, nutrient-poor, and low in salinity due to excess rainfall (Wyrtki, 1967). This is derived from the same water mass that is responsible for the lowered productivity at the Galapagos site.

The hydrographic data from site C is plotted in Fig. A I-8. Significant features are the presence of warm, saline Equatorial Surface Water and the indication of the Equatorial Undercurrent in the decrease in the thermocline gradient between 100 and 300 meters. The effect of the relatively oxygenated undercurrent can be seen in the elevated concentration of oxygen which is mixed down into the minimum layer which has much less oxygen to the north and south of the equator

Figure A I-7. MANOP sample locations - sites C and S.

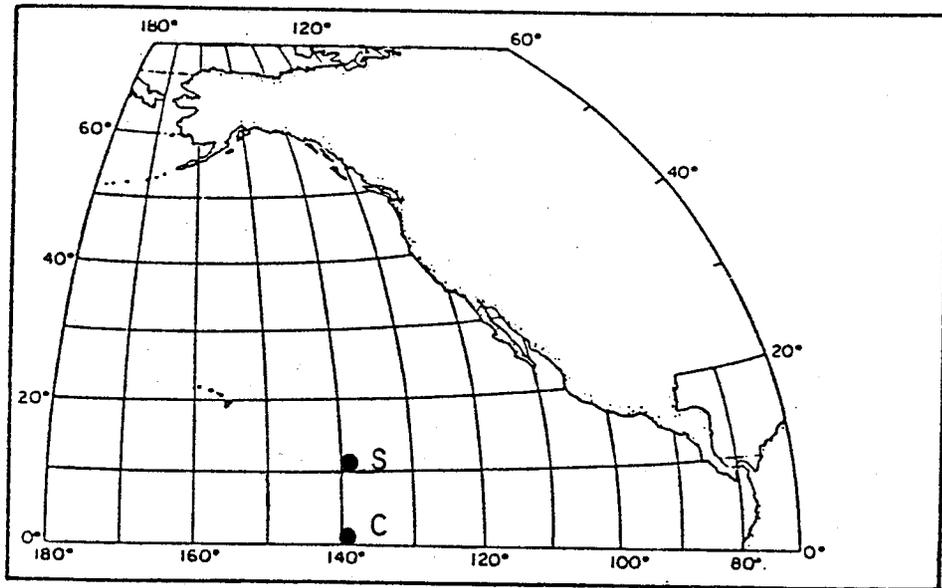
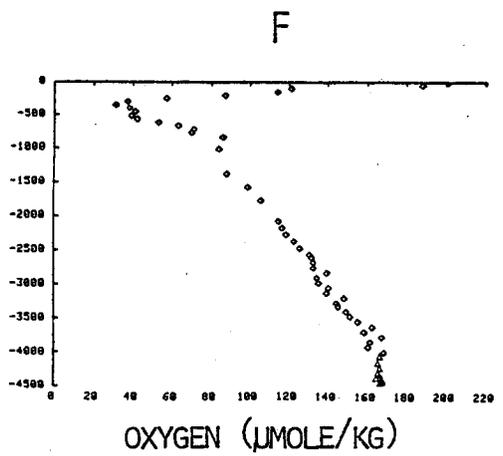
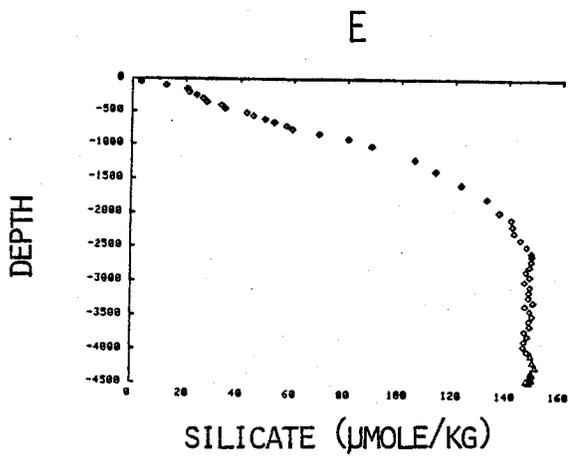
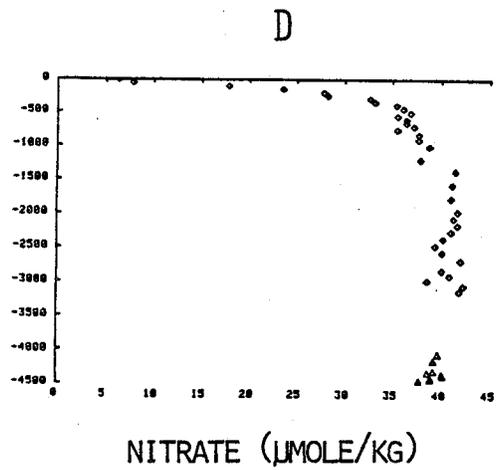
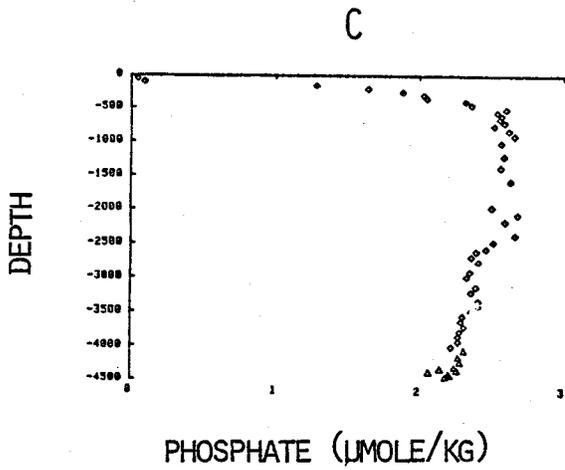
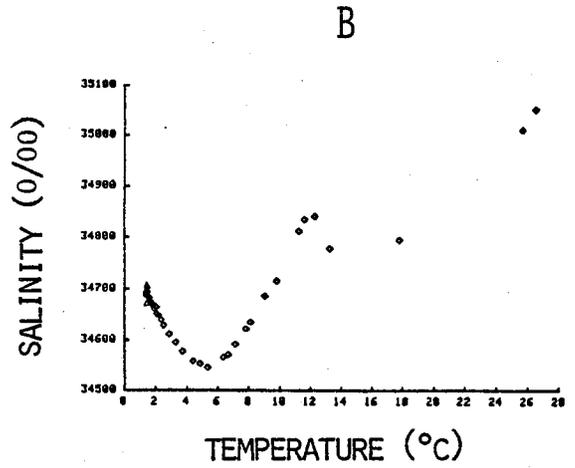
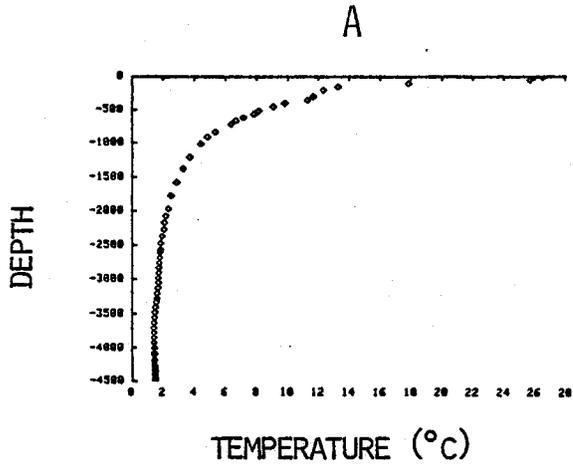


Figure A I-8. MANOP hydrographic data - site C.



(Reid, 1965). The profiles of Cu, Ni, and Cd are plotted in Fig. A I-9. The general features are the same as observed in other locations with a few exceptions. The level of Ni in the deep water never reaches the expected values over 11 nm/kg. Within the  $PO_4$ ,  $NO_3$  maximum, the concentration of Cd does not reach the same relative enrichment as the nutrients and the total concentration appears low. Some of these apparent inconsistencies may be related to problems in standardization and recovery consistency between analytical runs which have not been properly accounted for.

The hydrographic data at site S are shown in Fig. A I-10. The low salinity Tropical Surface Water carried by the Equatorial Countercurrent and the southern part of the North Equatorial Current can be seen in the surface layer. The intermediate water at this station is nearly in the core of the tongue of extremely low oxygen water extending to the west from the eastern margin of the Pacific. The extrema in nutrients and oxygen in this water are developed through horizontal diffusion and in-situ oxidation of organic matter produced under regions of high productivity which intensify progressively towards the east (Anderson, 1979). This water mass has a very long isolation time, situated between the North Pacific anticyclonic and Equatorial circulations (Wyrтки, 1967). The trace metal profiles are shown in Fig. A I-11. Again, the general form is similar to the other Pacific profiles with the same exceptions noted for site C - the Ni appears to be low and the Cd does not follow the intensity of the nutrient maxima. The Cd:P atom ratio is well below  $3.5 \times 10^{-4}$  throughout the thermocline and oxygen minimum. Only below the

Figure A I-9. MANOP dissolved Cu, Ni, Cd profiles - site C.

Line on Cd-P figure indicates deep Pacific regression with a Cd/P slope of  $0.35 \times 10^{-3}$  (Boyle et al., 1976; Bruland, 1980).

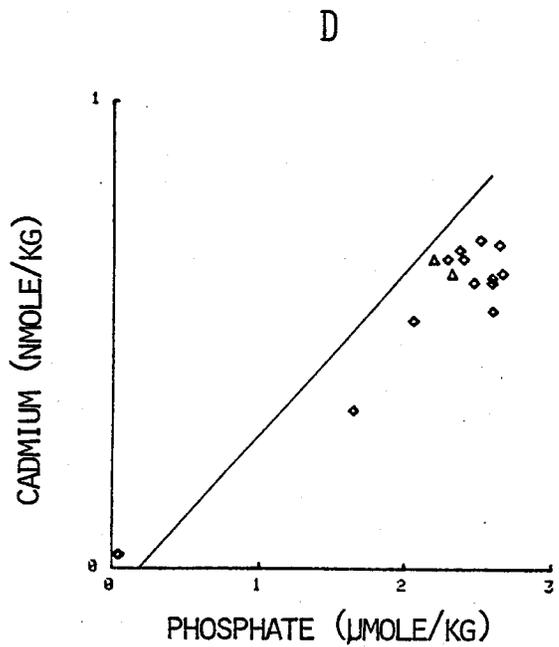
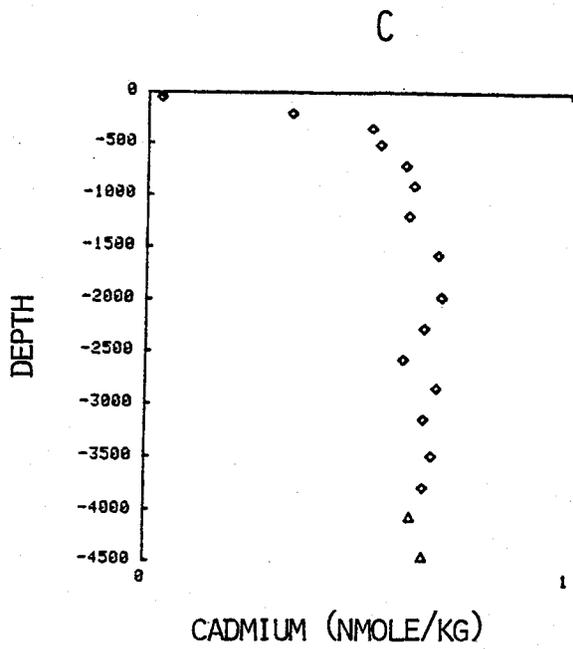
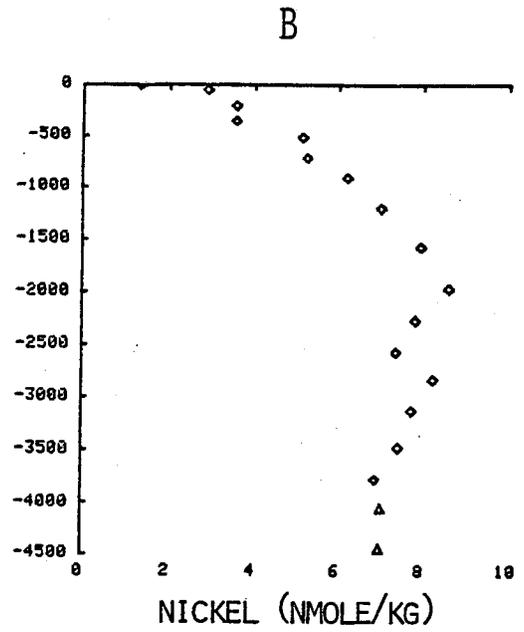
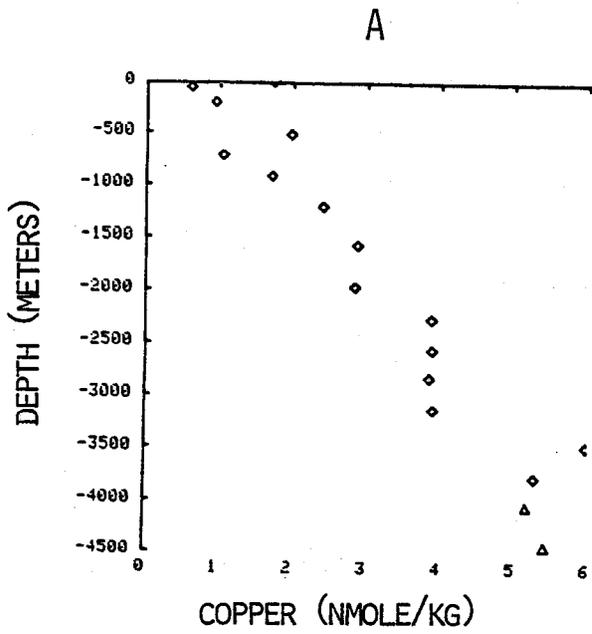


Figure A I-10. MANOP hydrographic data - site S.

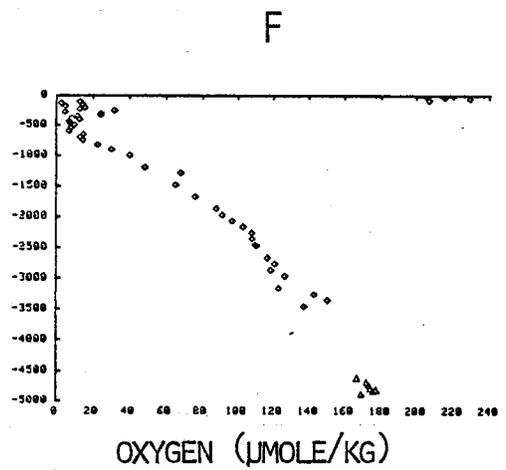
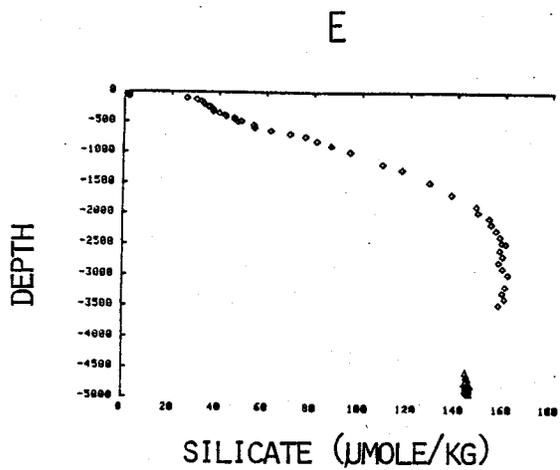
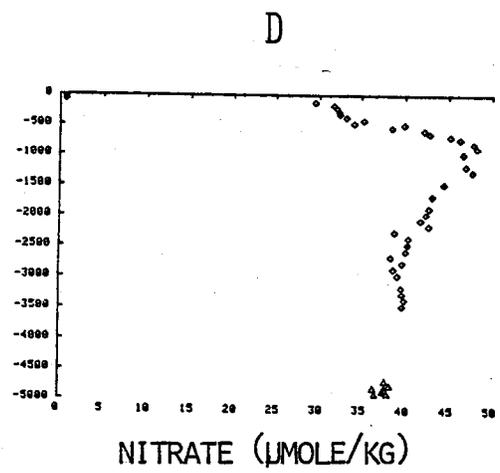
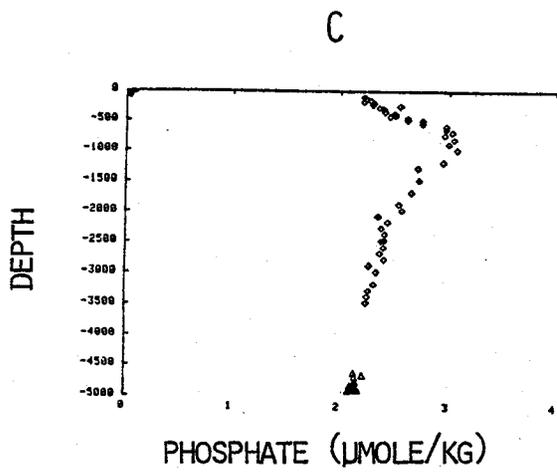
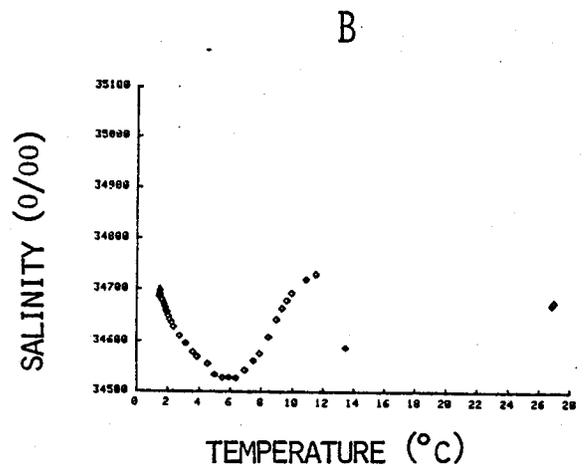
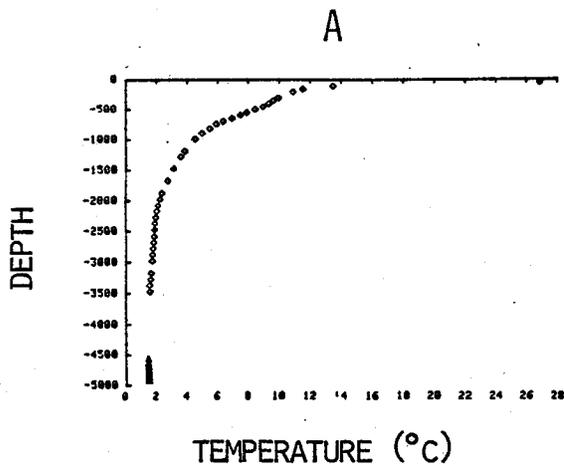
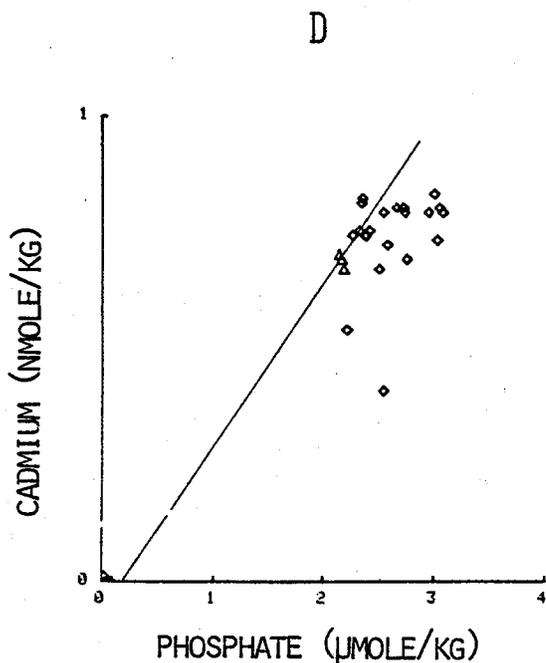
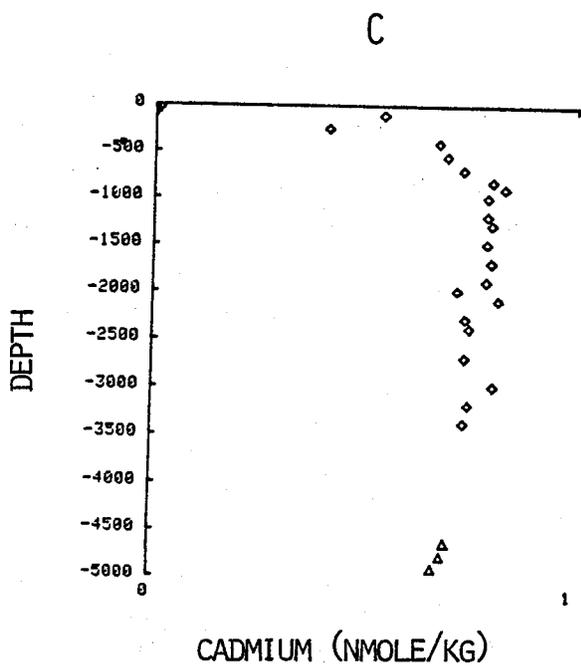
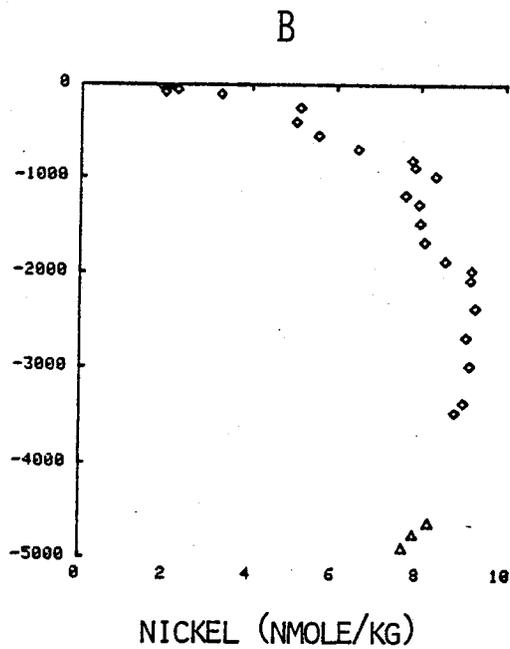
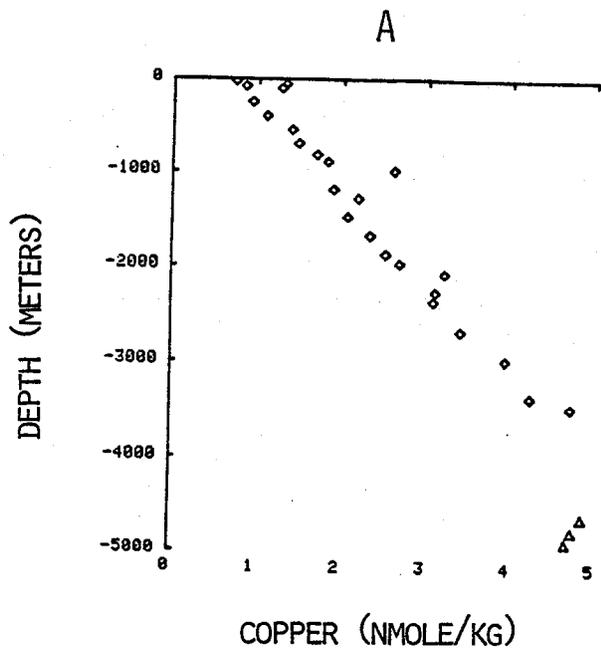


Figure A I-11. MANOP dissolved Cu, Ni, Cd profiles - site S.

Line on Cd-P figure indicates deep Pacific regression  
with a Cd/P slope of  $0.35 \times 10^{-3}$  (Boyle et al., 1976;  
Bruland, 1980).



intermediate water nutrient maximum does the ratio approach that measured in other non-Equatorial profiles. This seems to be a consistent feature of all of the Equatorial Pacific Water Mass (Sverdrup et al., 1959) and will be investigated further.

As already mentioned, all of the Pacific stations sampled were located within relatively productive water supported by the upwelled waters in the Equatorial current systems. Site C is in a band of very intense primary production which can be estimated from charts of Bogorov (1968) to be greater than  $250 \text{ mg C/m}^2\text{-day}$ . During the summer months when site S was occupied, the seasonal divergence between the Countercurrent and the west-flowing North Equatorial Current is very weak. The associated decrease in the upwelling supply of nutrients causes a drop in productivity from 150 to  $100 \text{ mg C/m}^2\text{-day}$  (El Sayed and Taguchi, 1979). This is still a relatively high rate of production for an open ocean station but it is definitely on the margin between the equatorial and central gyre environments.

The standing crop of plankton at site S was much lower than at site C judging from the significant difficulty in collecting enough material by hand tows at S. Details of the tows and the surface waters at the two sites are given in Table A I-3. Besides a decrease in the standing stock at S, there were relatively fewer siliceous organisms (radiolarians and diatoms) compared to other species and the  $\text{CaCO}_3/\text{SiO}_2$  ratio in the bulk tow at S was lower than that at C by at least a factor of ten. In these, and the Galapagos plankton tows, the mass of the collected biogenic material was dominated by Crustacea, with mixed, secondary populations of Pteropoda, Radiolaria,

Table A I-3. Central Pacific Samples - Description of Tows.

- Towed from Zodiac and boom extended forward from the R/V Knorr's direction of travel.
- Daytime tows, Zodiac:vertical tows from 5-75 meters; ship: horizontal tows at approx. 20 meters, 1 knot, 45 minutes.

SITE C:

TOW 1 - 5/12/79	approx. 100ml wet volume,	Zodiac.
TOW 2 - 5/14/79	120ml	Zodiac.

SITE S:

TOW 3 - 5/19/79	50ml	Zodiac.
TOW 5 - 5/24/79	50ml	Zodiac.
TOW 6 - 5/25/79	90ml	Ship.
TOW 7 - 5/26/79	100ml	Ship.

All tows at each site were similar in their relative distributions of organisms and are described below in order of decreasing mass contribution (estimated).

Site C - Copepoda - large variety of adults and nauplii.  
Lesser numbers of Diatoms, Acantharia, Pteropods, and Forams.

Site S - Crustacea - by far the largest mass in the tow.  
Much smaller numbers of Pteropods and Radiolaria.

Surface water properties:

STN	T	PO <sub>4</sub>	NO <sub>3</sub>	Si	Cu	Ni	Cd
C	26.5	.042 $\mu$ M	7.1 $\mu$ M	3.2 $\mu$ M	.72 nM	2.44 nM	.016 nM
S	27.0	.027	0.7	1.9	.75	1.94	.010

Foraminifera, Coccolithophorids, and Diatoms.

The sediments under these sites again reflect the extension of the equatorial upwelling productivity discussed for the Galapagos site as calcareous and siliceous tests dominate the mass and distribution of sedimentary material (van Andel et al,1975). The very central tongue of high productivity is underlain by a thick deposit of calcareous ooze. This grades to siliceous ooze further to the north where the drop in surface productivity reduces the supply of  $\text{CaCO}_3$  and the CCD shoals. Further to the north the sediments grade into the slowly accumulating central gyre red clays. Unlike the Galapagos sediments in the Panama Basin, the distribution of opal on a carbonate-free basis follows the details of the surface productivity distribution quite closely. Specifically, site C has sediments that are greater than 70% by weight  $\text{CaCO}_3$  - primarily foraminifera and nanofossils with smaller numbers of diatoms and radiolarians making up the balance (Lyle and Heath,1979). The sedimentation rate is uniform and relatively high at 1.0 to 1.2 cm/1000 years. The sediments at site S are much more complicated and show relatively high horizontal heterogeneity. The modern surface material is primarily radiolarian ooze with varying mixtures of clay and manganese nodules. The overall sedimentation rate is much lower than at C and there are outcrops and highly burrowed mixtures of modern and tertiary materials (Lyle,1980).

Appendix II Analytical data for samples and leaches.

-Each entry in the table represents one particulate matter sample or a leaching solution.

KEY:

Sampling location

Sample type 1,2,3 -

- 1 Filters - since these were subsampled into various masses the elements are reported as conc./gram dry plankton.
- 2 Tubes - total element detected in that solubilized tube.
- 3 Leaches - total element in that leaching solution.

Sample volume (ml) -

particulate matter (filter, tubes) - volume of solubilized material.  
leaches - volume of total leaching solutions - in cases where these are composite solutions from several tubes, the volume is the volume per tube (total vol/# tubes)

Sample mass (mg) -

filters - total mass on filter  
tubes - total mass estimate for original tube based on filters and chemical analyses.  
leaches - total mass in original tube exposed to leaching soln.

Elements -

mmoles - Ca, P, Si, C, N  
umoles - Fe, Zn, Al  
nmoles - Cu, Ni, Cd, Mn, Ba

---

\*

organic extraction samples and filtered seawater samples have elements reported in conc/per ml soln.

Antarctic

A10

type: 1  
volume: 3.01  
mass: 116

Ca 0.011  
P 0.0238  
Si  
C  
N  
Cu 46.5 ( 3.3)  
Ni 16.3  
Cd 1.65  
Fe 0.17 ( 0.025)  
Mn  
Zn 0.583  
Al  
Ba

Antarctic

A7

type: 1  
volume: 3.01  
mass: 81

Ca 0.23  
P  
Si  
C  
N  
Cu 297 ( 10)  
Ni 19.2 ( 3)  
Cd 20  
Fe 2.53 ( 0.22)  
Mn  
Zn 6.06  
Al  
Ba

Antarctic

A4

type: 1  
volume: 3.01  
mass: 80

Ca 0.41  
P 0.214  
Si  
C  
N  
Cu 410 ( 12)  
Ni 63 ( 6)  
Cd 98  
Fe 2.73 ( 0.23)  
Mn  
Zn 3.75  
Al  
Ba

Antarctic

T3

type: 2  
volume: 15  
mass: 167

Ca  
P  
Si 2.05  
C  
N  
Cu  
Ni  
Cd  
Fe .026 (.004)  
Mn  
Zn .053 (.003)  
Al .068 (.007)  
Ba 34 ( 15)

Antarctic

T19

type: 2  
volume: 15  
mass: 167

Ca  
P  
Si  
C  
N  
Cu  
Ni  
Cd  
Fe .013 (.002)  
Mn  
Zn .038 (.005)  
Al .057 (.003)  
Ba 22 ( 3)

Antarctic

T26

type: 2  
volume: 15  
mass: 167

Ca  
P  
Si  
C  
N  
Cu  
Ni  
Cd  
Fe .038 (.003)  
Mn  
Zn .0058 (.0004)  
Al .052 (.010)  
Ba 0.4 ( 0.1)

Galapagos

GA200

type: 1  
volume: 2  
mass: 97

Ca 0.89  
P 0.213  
Si 1.27  
C 32.1  
N 6  
Cu 150 ( 6)  
Ni 200 ( 30)  
Cd 400 ( 50)  
Fe 4.9 ( 0.1)  
Mn 150 ( 30)  
Zn 1.2 ( 0.09)  
Al 9 ( 1.8)  
Ba

Galapagos

GA201

type: 1  
volume: 2  
mass: 118

Ca 0.83  
P 0.213  
Si 1.26  
C 34.6  
N 6.35  
Cu 160 ( 15)  
Ni 200 ( 20)  
Cd 670 ( 50)  
Fe 5.4 ( 0.1)  
Mn 200 ( 20)  
Zn 1.55 ( 0.16)  
Al  
Ba

Galapagos

T91

type: 2  
volume: 6  
mass: 174

Ca 0.115  
P 0.0205  
Si  
C  
N  
Cu 20.8 ( 0.5)  
Ni 29.7 ( 2.4)  
Cd 27.9 ( 2.6)  
Fe 1.185 ( 0.072)  
Mn 13 ( 0.2)  
Zn 0.165 ( 0.007)  
Al  
Ba

Galapagos

T98

type: 2  
volume: 6  
mass: 158

Ca 0.128  
P 0.0412  
Si  
C  
N  
Cu 35.8 ( 0.6)  
Ni 31.5 ( 1.2)  
Cd 38.5 ( 4.5)  
Fe 1.043 ( 0.079)  
Mn 22.4 ( 0.6)  
Zn 0.197 ( 0.029)  
Al  
Ba

Galapagos

167

type: 3  
volume: 25  
mass: 166

Ca 0  
P 0.0275  
Si 0.0015  
C  
N  
Cu 6.4 ( 1)  
Ni 5 ( 0.6)  
Cd 23 ( 2.6)  
Fe 0.0046 ( 9.0E-4)  
Mn 3.4 ( 0.6)  
Zn 0.0178 ( 0.0019)  
Al 0  
Ba

Galapagos

158

type: 3  
volume: 47  
mass: 174

Ca 0.0246  
P 0.0183  
Si 0.0026  
C  
N  
Cu 4.8 ( 0.6)  
Ni 5.9 ( 0.7)  
Cd 19.4 ( 1.4)  
Fe 0.0171 ( 0.0021)  
Mn 6.8 ( 0.7)  
Zn 0.02 ( 0.0013)  
Al 0  
Ba

Galapagos

160

type: 3  
volume: 46  
mass: 174

Ca 0.008  
P 0.0083  
Si 0.0021  
C  
N  
Cu 3.3 ( 0.2)  
Ni 1.8 ( 0.2)  
Cd 16.7 ( 2.8)  
Fe 0.026 ( 0.003)  
Mn 3.5 ( 0.5)  
Zn 0.0192 ( 1.0E-3)  
Al 0  
Ba

Galapagos

T86

type: 2  
volume: 6  
mass: 167

Ca 0.098  
P 0.00804  
Si  
C  
N  
Cu 22 ( 0.9)  
Ni 21.8 ( 1.8)  
Cd 30.8 ( 2.5)  
Fe 1.083 ( 0.043)  
Mn 8.5 ( 0.2)  
Zn 0.177 ( 0.01)  
Al  
Ba

Galapagos

154

type: 3  
volume: 32  
mass: 167

Ca 0.008  
P 0.0608  
Si 0.0049  
C  
N  
Cu 5.6 ( 0.9)  
Ni 13.3 ( 1.9)  
Cd 45.7 ( 3.2)  
Fe 0.0105 ( 9.0E-4)  
Mn 14.2 ( 1.2)  
Zn 0.031 ( 0.005)  
Al 0  
Ba

Galapagos

165

type: 3  
volume: 46  
mass: 167

Ca 0.005  
P 0.0079  
Si 0.0017  
C  
N  
Cu 1.8 ( 0.1)  
Ni 1.7 ( 0.2)  
Cd 5.63 ( 0.47)  
Fe 0.024 ( 0.0019)  
Mn 3.5 ( 0.2)  
Zn 0.015 ( 0.0013)  
Al 0  
Ba

Galapagos

194

type: 3  
volume: 43  
mass: 167

Ca  
P 0.0022  
Si 0.0014  
C  
N  
Cu 0.1  
Ni 1 ( 0.4)  
Cd 0.73 ( 0.06)  
Fe 0.0035 ( 9.0E-4)  
Mn 0.26 ( 0.03)  
Zn 0.017 ( 0.0011)  
Al  
Ba

Galapagos

GA204

type: 1  
volume: 2  
mass: 100

Ca 0.77  
P 0.16  
Si 0.68  
C 36.8  
N 6.25  
Cu 175 ( 6)  
Ni 130 ( 12)  
Cd 570 ( 35)  
Fe 2.8 ( 0.1)  
Mn 90 ( 7)  
Zn 2.14 ( 0.31)  
Al 7.8 ( 1.3)  
Ba

Galapagos

132

type: 3  
volume: 44.9  
mass: 160

Ca 0.0102  
P 0.016  
Si 4.5E-4  
C  
N  
Cu 3.4 ( 0.1)  
Ni 4.4 ( 0.4)  
Cd 5.7 ( 0.3)  
Fe 0.0202 ( 0.0011)  
Mn 5.1 ( 0.2)  
Zn 0.015 ( 0.0015)  
Al 0.0028 ( 0.1)  
Ba 3.8 ( 0.5)

Galapagos

131

type: 3  
volume: 43.9  
mass: 162

Ca 0.0083  
P 0.015  
Si 4.2E-4  
C  
N  
Cu 3.1 ( 0.1)  
Ni 3.9 ( 0.7)  
Cd 5.7 ( 0.3)  
Fe 0.019 ( 1.0E-3)  
Mn 4.9 ( 0.2)  
Zn 0.012 ( 8.0E-4)  
Al 0.0017 ( 3.0E-4)  
Ba

Galapagos

149

type: 3  
volume: 45.1  
mass: 160

Ca 0.0205  
P 0.006  
Si 9.5E-4  
C  
N  
Cu 1.5 ( 0.1)  
Ni 5.9 ( 0.5)  
Cd 2.6 ( 0.1)  
Fe 0.0091 ( 7.0E-4)  
Mn 3.2 ( 0.2)  
Zn 0.03 ( 0.0016)  
Al 0.0025 ( 3.0E-4)  
Ba 6.6 ( 1)

Galapagos

130

type: 3  
volume: 46.6  
mass: 162

Ca 0.0201  
P 0.007  
Si 9.8E-4  
C  
N  
Cu 1.8 ( 0.1)  
Ni 6.6 ( 0.5)  
Cd 2.9 ( 0.1)  
Fe 0.01 ( 5.0E-4)  
Mn 3.2 ( 0.1)  
Zn 0.028 ( 0.0014)  
Al 0.0025 ( 2.0E-4)  
Ba

Galapagos

135

type: 3  
volume: 44.5  
mass: 160

Ca .184  
P 0.002  
Si 1.1E-4  
C  
N  
Cu 14 ( 0.4)  
Ni 14 ( 1)  
Cd 36.1 ( 5.2)  
Fe 0.057 ( 0.002)  
Mn 4.4 ( 0.24)  
Zn 0.125 ( 0.019)  
Al 0.044 ( 0.006)  
Ba 36 ( 6)

Galapagos

118

type: 3  
volume: 45.2  
mass: 162

Ca .194  
P 0.002  
Si 1.1E-4  
C  
N  
Cu 14 ( 0.7)  
Ni 13 ( 0.7)  
Cd 27.3 ( 2.6)  
Fe 0.05 ( 0.002)  
Mn 4.6 ( 0.2)  
Zn 0.13 ( 0.014)  
Al 0.037 ( 0.011)  
Ba

Galapagos

129

type: 3  
volume: 24.9  
mass: 161

Ca 0.0024  
P 0.008  
Si  
C  
N  
Cu 13 ( 0.3)  
Ni 5 ( 0.3)  
Cd 1.5 ( 0.1)  
Fe 0.216 ( 0.009)  
Mn 1.9 ( 0.4)  
Zn 0.031 ( 0.003)  
Al 0.075 ( 0.009)  
Ba 29 ( 2)

Galapagos

125

type: 3  
volume: 17.3  
mass: 161

Ca 0.0026  
P 0.026  
Si 5.2E-4  
C  
N  
Cu 5.02 ( 0.37)  
Ni 7.9 ( 0.9)  
Cd 9.9 ( 0.8)  
Fe 0.0216 ( 0.0011)  
Mn 8.9 ( 0.3)  
Zn 0.021 ( 0.0017)  
Al 0.0024 ( 3.0E-4)  
Ba 2.7 ( 0.6)

MANOP C

GA217

type: 1  
volume: 10  
mass: 99

Ca  
P  
Si 0.0457  
C  
N  
Cu  
Ni  
Cd  
Fe  
Mn  
Zn  
Al  
Ba

MANOP C

T47

type: 2  
volume: 15  
mass: 173

Ca 0.253  
P 0.0297  
Si  
C  
N  
Cu 14.5 ( 1.5)  
Ni 18.7 ( 1.5)  
Cd 15.3 ( 0.8)  
Fe 0.2 ( 0.018)  
Mn 10.5 ( 1)  
Zn 0.188 ( 0.007)  
Al 0.124 ( 0.015)  
Ba

MANOP C

T48

type: 2  
volume: 15  
mass: 194

Ca 0.197  
P 0.0237  
Si  
C  
N  
Cu 14.7 ( 1)  
Ni 24.4 ( 0.7)  
Cd 16.2 ( 0.8)  
Fe 0.214 ( 0.019)  
Mn 8.3 ( 0.9)  
Zn 0.31 ( 0.013)  
Al 0.176 ( 0.027)  
Ba

MANOP C

T49

type: 2  
volume: 15.2  
mass: 204

Ca 0.312  
P 0.043  
Si  
C  
N  
Cu 21.1 ( 1.4)  
Ni 48.6 ( 3)  
Cd 23.7 ( 0.5)  
Fe 0.252 ( 0.009)  
Mn 17.3 ( 0.9)  
Zn 0.193 ( 0.01)  
Al 0.172 ( 0.015)  
Ba

MANOP C

X186

type: 3  
volume: 22.2  
mass: 194

Ca 0  
P 0.0143  
Si  
C  
N  
Cu 3.7 ( 0.9)  
Ni 7.3 ( 0.9)  
Cd 7.6 ( 0.2)  
Fe 0.0157 ( 0.0025)  
Mn 2.7 ( 0.7)  
Zn  
Al  
Ba

MANOP C

X197

type: 3  
volume: 32.34  
mass: 173

Ca 0.0032  
P 0.0247  
Si  
C  
N  
Cu 3.5 ( 0.6)  
Ni 12.4 ( 1.6)  
Cd 4.72 ( 0.23)  
Fe 0.0169 ( 0.0029)  
Mn 5.6 ( 1.4)  
Zn  
Al  
Ba

MANOP C

X198

type: 3  
volume: 32.72  
mass: 194

Ca 0.0033  
P 0.0091  
Si  
C  
N  
Cu 6.8 ( 1.3)  
Ni 21.2 ( 2.2)  
Cd 9.3 ( 0.5)  
Fe 0.0157 ( 0.0037)  
Mn 5.7 ( 0.8)  
Zn  
Al  
Ba

MANOP C

X177

type: 3  
volume: 1  
mass: 8.74

Ca  
P 4.92E-4  
Si  
C  
N  
Cu 0.06 ( 0.007)  
Ni 0.35 ( 0.04)  
Cd 0.086 ( 0.018)  
Fe 3.1E-4 ( 5.0E-5)  
Mn 0.09 ( 0.005)  
Zn  
Al  
Ba

MANOP C

GA220

type: 1  
volume: 10  
mass: 42

Ca  
P  
Si 0.01275  
C  
N  
Cu  
Ni  
Cd  
Fe  
Mn  
Zn  
Al  
Ba

MANOP C

T42

type: 2  
volume: 15.3  
mass: 180

Ca 0.312  
P 0.0444  
Si  
C  
N  
Cu 25.4 ( 1.2)  
Ni 33.4 ( 1.4)  
Cd 25.1 ( 0.6)  
Fe 0.363 ( 0.017)  
Mn 16.5 ( 0.5)  
Zn 0.151 ( 0.006)  
Al 0.287 ( 0.05)  
Ba 93 ( 14)

MANOP C

T43

type: 2  
volume: 15  
mass: 126

Ca 1.1E-4  
P 0.00392  
Si  
C  
N  
Cu 0.27 ( 0.03)  
Ni 0.48 ( 0.23)  
Cd 0  
Fe 0.0788 ( 0.006)  
Mn 0.36 ( 0.03)  
Zn 0.008 ( 1.0E-3)  
Al 0.0426 ( 0.006)  
Ba 0.8 ( 0.06)

MANOP C

T44

type: 2  
volume: 15  
mass: 108

Ca 2.0E-5  
P 6.6E-4  
Si  
C  
N  
Cu 0.15 ( 0.05)  
Ni 0.11 ( 0.11)  
Cd 0  
Fe 0.0371 ( 0.002)  
Mn 0.11 ( 0.03)  
Zn 0.0054 ( 6.0E-4)  
Al 0.016 ( 1.0E-3)  
Ba 0.3 ( 0.05)

MANOP C

X185

type: 3  
volume: 17.77  
mass: 180

Ca 0  
P 0.00753  
Si  
C  
N  
Cu 2.56 ( 0.32)  
Ni 1.23 ( 0.18)  
Cd 1.16 ( 0.05)  
Fe 0.00578 ( 9.8E-4)  
Mn 1.26 ( 0.11)  
Zn  
Al  
Ba

MANOP C

X188

type: 3  
volume: 17.88  
mass: 117

Ca 0  
P 0.0045  
Si  
C  
N  
Cu 1.79 ( 0.18)  
Ni 4.34 ( 0.64)  
Cd 1.11 ( 0.02)  
Fe 0.00545 ( 1.1E-4)  
Mn 0.95 ( 0.07)  
Zn  
Al 0.006 ( 0.004)  
Ba 4.9 ( 0.59)

MANOP C

X178

type: 3  
volume: 30.3  
mass: 117

Ca  
P  
Si  
C  
N  
Cu  
Ni  
Cd 0.26 ( 0.03)  
Fe  
Mn  
Zn  
Al  
Ba

MANOP C

X185

type: 3  
volume: 17.77  
mass: 180

Ca 0  
P 0.00753  
Si  
C  
N  
Cu 2.56 ( 0.32)  
Ni 1.23 ( 0.18)  
Cd 1.16 ( 0.05)  
Fe 0.00578 ( 9.8E-4)  
Mn 1.26 ( 0.11)  
Zn  
Al  
Ba

MANOP C

X188

type: 3  
volume: 17.88  
mass: 117

Ca 0  
P 0.0045  
Si  
C  
N  
Cu 1.79 ( 0.18)  
Ni 4.34 ( 0.64)  
Cd 1.11 ( 0.02)  
Fe 0.00545 ( 1.1E-4)  
Mn 0.95 ( 0.07)  
Zn  
Al 0.006 ( 0.004)  
Ba 4.9 ( 0.59)

MANOP C

X178

type: 3  
volume: 30.3  
mass: 117

Ca  
P  
Si  
C  
N  
Cu  
Ni  
Cd 0.26 ( 0.03)  
Fe  
Mn  
Zn  
Al  
Ba

MANOP C

X184

type: 3  
volume: 32.66  
mass: 126

Ca 0  
P 0.012  
Si 3.05E-4  
C  
N  
Cu 4.7 ( 0.2)  
Ni 10.2 ( 1)  
Cd 4.41 ( 0.16)  
Fe 0.012 ( 1.0E-3)  
Mn 3.43 ( 0.16)  
Zn 0.0174 ( 0.0023)  
Al 0.0027 ( 7.0E-4)  
Ba

MANOP C

X175

type: 3  
volume: 33.38  
mass: 108

Ca 0.011  
P 0.0233  
Si 8.14E-4  
C  
N  
Cu 4.2 ( 0.3)  
Ni 14.4 ( 0.7)  
Cd 5.44 ( 0.28)  
Fe 0.013 ( 1.0E-3)  
Mn 5.64 ( 0.47)  
Zn 0.0148 ( 9.0E-4)  
Al 0.0022 ( 0.0013)  
Ba 10.8 ( 1.1)

MANOP C

X189

type: 3  
volume: 31.61  
mass: 126

Ca 0.009  
P 0.00221  
Si 1.01E-4  
C  
N  
Cu 1.8 ( 0.4)  
Ni 1.6 ( 0.7)  
Cd 1.58 ( 0.09)  
Fe 0.0021 ( 2.0E-4)  
Mn 1.61 ( 0.19)  
Zn 0.00714 ( 3.5E-4)  
Al  
Ba

MANOP C

X172

type: 3  
volume: 31.41  
mass: 108

Ca 0.016  
P 0.00119  
Si 7.04E-4  
C  
N  
Cu 1 ( 0.08)  
Ni 1.6 ( 0.3)  
Cd 1.22 ( 0.09)  
Fe 0.0015 ( 2.0E-4)  
Mn 1.01 ( 0.09)  
Zn 0.0081 ( 5.7E-4)  
Al  
Ba 4.2 ( 0.5)

MANOP C  
X180  
type: 3  
volume: 31.82  
mass: 126  
Ca 0.145  
P 5.1E-4  
Si 2.03E-4  
C  
N  
Cu 9.5 ( 0.5)  
Ni 9.2 ( 0.4)  
Cd 9.29 ( 0.29)  
Fe 0.015 ( 0.002)  
Mn 4.01 ( 0.13)  
Zn 0.0481 ( 0.0022)  
Al 0.032 ( 0.005)  
Ba

MANOP C  
X169  
type: 3  
volume: 31.5  
mass: 108  
Ca 0.135  
P 1.6E-4  
Si 1.73E-4  
C  
N  
Cu 8.5 ( 0.5)  
Ni 4.3 ( 0.4)  
Cd 8.13 ( 0.13)  
Fe 0.0069 ( 0.0014)  
Mn 2.05 ( 0.13)  
Zn 0.0362 ( 0.0013)  
Al 0.037 ( 0.002)  
Ba 13.9 ( 2)

MANOP C  
X168  
type: 3  
volume: 23.38  
mass: 126  
Ca 0.0035  
P 0.0134  
Si 4.44E-4  
C  
N  
Cu 5.2 ( 0.2)  
Ni 1.2 ( 0.2)  
Cd 0.54 ( 0.02)  
Fe 0.062 ( 0.003)  
Mn 1.03 ( 0.05)  
Zn 0.00374 ( 1.2E-4)  
Al 0.049 ( 0.002)  
Ba

MANOP C  
X176  
type: 3  
volume: 24.05  
mass: 108  
Ca 0.0013  
P 0.0038  
Si 7.5E-4  
C  
N  
Cu 1.3 ( 0.1)  
Ni 0.46 ( 0.17)  
Cd 0.22 ( 0.02)  
Fe 0.06 ( 0.002)  
Mn 0.7 ( 0.03)  
Zn 0.00289 ( 1.0E-4)  
Al 0.031 ( 0.003)  
Ba 2.34 ( 0.4)

MANOP C

X171

type: 3  
volume: 1  
mass: 6.54

Ca  
P 2.04E-4  
Si  
C  
N  
Cu 0.064 ( 0.009)  
Ni 0.136 ( 0.014)  
Cd 0.068 ( 0.004)  
Fe  
Mn 0.047 ( 0.005)  
Zn  
Al  
Ba

MANOP C

X183

type: 3  
volume: 1  
mass: 6.54

Ca  
P 3.32E-4  
Si  
C  
N  
Cu 0.08 ( 0.013)  
Ni 0.18 ( 0.013)  
Cd 0.112 ( 0.005)  
Fe  
Mn 0.055 ( 0.005)  
Zn  
Al  
Ba

MANOP C

X182

type: 3  
volume: 1  
mass: 6.54

Ca  
P 1.82E-4  
Si  
C  
N  
Cu 0.027 ( 0.013)  
Ni 0.094 ( 0.018)  
Cd 0.012 ( 0.005)  
Fe  
Mn 0.04 ( 0.004)  
Zn  
Al  
Ba

MANOP C

X163

type: 3  
volume: 1  
mass: 6.54

Ca  
P 1.75E-4  
Si  
C  
N  
Cu 0.069 ( 0.009)  
Ni 0.091 ( 0.017)  
Cd 0.015 ( 0.002)  
Fe  
Mn 0.034 ( 0.017)  
Zn  
Al  
Ba

MANOP S

GA222

type: 1  
volume: 5  
mass: 22

Ca  
P  
Si 0.00259  
C  
N  
Cu  
Ni  
Cd  
Fe  
Mn  
Zn  
Al  
Ba

MANOP S

T37

type: 2  
volume: 15  
mass: 71

Ca 0.273  
P 0.0176  
Si  
C  
N  
Cu 14.8 ( 0.9)  
Ni 20.2 ( 1.1)  
Cd 9.45 ( 0.51)  
Fe 0.566 ( 0.049)  
Mn 7.3 ( 0.3)  
Zn 0.095 ( 0.004)  
Al 0.915 ( 0.105)  
Ba

MANOP S

T40

type: 2  
volume: 15.2  
mass: 67

Ca 0.233  
P 0.018  
Si  
C  
N  
Cu 16 ( 1.5)  
Ni 19.5 ( 0.9)  
Cd 13.4 ( 0.3)  
Fe 0.478 ( 0.018)  
Mn 10.5 ( 0.5)  
Zn 0.093 ( 0.009)  
Al 0.82 ( 0.05)  
Ba

MANOP S

X110

type: 3  
volume: 18.9  
mass: 69

Ca 0  
P 0.00457  
Si  
C  
N  
Cu 1.83 ( 0.42)  
Ni 2.49 ( 0.45)  
Cd 1.98 ( 0.23)  
Fe 0.00839 ( 0.00173)  
Mn 2.04 ( 0.34)  
Zn  
Al  
Ba

MANOP S  
X123  
type: 3  
volume: 22.02  
mass: 71  
Ca 0  
P 0.00821  
Si  
C  
N  
Cu 3.17 ( 0.53)  
Ni 6.21 ( 1.59)  
Cd 10.2 ( 0.5)  
Fe 0.0182 ( 0.0032)  
Mn 4.62 ( 1.06)  
Zn  
Al  
Ba

MANOP S  
X117  
type: 3  
volume: 22.54  
mass: 67  
Ca 0  
P 0.00791  
Si  
C  
N  
Cu 3.02 ( 0.59)  
Ni 3.25 ( 1.62)  
Cd 6.51 ( 0.45)  
Fe 0.00825 ( 0.00135)  
Mn 2.03 ( 0.41)  
Zn  
Al  
Ba

MANOP S  
T34  
type: 2  
volume: 15  
mass: -1.0E+99  
Ca 0.185  
P 0.0087  
Si  
C  
N  
Cu 10.3 ( 0.7)  
Ni 22.1 ( 1.1)  
Cd 5.1 ( 0.3)  
Fe 0.171 ( 0.0075)  
Mn 10.7 ( 0.9)  
Zn 0.0288 ( 0.003)  
Al 0.669 ( 0.036)  
Ba 19.8 ( 3.2)

MANOP S  
T35  
type: 2  
volume: 15  
mass: -1.0E+99  
Ca 0.132  
P 0.0095  
Si  
C  
N  
Cu 5.5 ( 0.4)  
Ni 22.4 ( 1.1)  
Cd 3.68 ( 0.36)  
Fe 0.186 ( 0.011)  
Mn 5.18 ( 0.41)  
Zn 0.045 ( 0.009)  
Al 0.51 ( 0.008)  
Ba 28 ( 3)

MANOP S  
X121  
type: 3  
volume: 5.37  
mass: -1.0E+99  
Ca  
P  
Si  
C  
N  
Cu 0.51 ( 0.11)  
Ni 7.3 ( 1.6)  
Cd 12 ( 2.7)  
Fe 0.003 ( 6.0E-4)  
Mn 5 ( 0.2)  
Zn  
Al  
Ba

MANOP S  
X128  
type: 3  
volume: 5.73  
mass: -1.0E+99  
Ca  
P  
Si  
C  
N  
Cu  
Ni 0.57 ( 0.29)  
Cd 1.72 ( 0.57)  
Fe 0.00372 ( 5.7E-4)  
Mn 0.17 ( 0.01)  
Zn  
Al  
Ba

MANOP S  
XT35  
type: 3  
volume: 5  
mass: -1.0E+99  
Ca  
P  
Si  
C  
N  
Cu  
Ni 0.57 ( 0.29)  
Cd 1.72 ( 0.57)  
Fe 0.00372 ( 5.7E-4)  
Mn 0.17 ( 0.01)  
Zn  
Al  
Ba

MANOP S  
XT34  
type: 3  
volume: 5  
mass: -1.0E+99  
Ca  
P  
Si  
C  
N  
Cu 0  
Ni 0  
Cd 0  
Fe 0  
Mn 0  
Zn  
Al  
Ba

MANOP S

X129

type: 3  
volume: 34.5  
mass: -1.0E+99

Ca  
P  
Si  
C  
N  
Cu 0.79 ( 0.35)  
Ni 5.5 ( 2.8)  
Cd 9 ( 2.8)  
Fe 0.0095 ( 0.0035)  
Mn 1.9 ( 0.1)  
Zn  
Al  
Ba

MANOP S

GA223

type: 1  
volume: 5  
mass: 53

Ca  
P  
Si 0.00361  
C  
N  
Cu  
Ni  
Cd  
Fe  
Mn  
Zn  
Al  
Ba

MANOP S

GA224

type: 1  
volume: 5  
mass: 31

Ca  
P  
Si 0.00326  
C  
N  
Cu  
Ni  
Cd  
Fe  
Mn  
Zn  
Al  
Ba

MANOP S

T30

type: 2  
volume: 15.1  
mass: 133

Ca 0.211  
P 0.0317  
Si  
C  
N  
Cu 15.9 ( 1.8)  
Ni 44.1 ( 1.5)  
Cd 25.8 ( 0.6)  
Fe 0.249 ( 0.014)  
Mn 13.9 ( 0.5)  
Zn 0.167 ( 0.009)  
Al 0.463 ( 0.06)  
Ba

MANOP S

X127

type: 3  
volume: 14.21  
mass: 133

Ca 0  
P 0.0166  
Si  
C  
N  
Cu 4.22 ( 0.26)  
Ni 13.6 ( 2.4)  
Cd 2.69 ( 0.14)  
Fe 0.0119 ( 1.0E-3)  
Mn 3.52 ( 0.31)  
Zn  
Al  
Ba

MANOP S

X136

type: 3  
volume: 14.92  
mass: 133

Ca 0  
P 0.0246  
Si  
C  
N  
Cu 2.37 ( 0.54)  
Ni 19.9 ( 1.8)  
Cd 4.64 ( 0.3)  
Fe 0.0186 ( 0.0012)  
Mn 6.46 ( 0.66)  
Zn  
Al  
Ba

MANOP S

X125

type: 3  
volume: 16.34  
mass: 133

Ca 0  
P 0.034  
Si  
C  
N  
Cu 1.91 ( 0.38)  
Ni 22.4 ( 1.7)  
Cd 6.96 ( 0.16)  
Fe 0.0253 ( 0.0014)  
Mn 8.42 ( 0.16)  
Zn  
Al  
Ba

MANOP S

X140

type: 3  
volume: 15.96  
mass: 133

Ca 0  
P 0.0389  
Si  
C  
N  
Cu 4.21 ( 0.34)  
Ni 26.9 ( 2.4)  
Cd 6.86 ( 0.35)  
Fe 0.0312 ( 0.0012)  
Mn 9.53 ( 0.24)  
Zn  
Al  
Ba

MANOP S

X76

type: 3  
volume: 16.89  
mass: 133

Ca 0  
P 0.0378  
Si  
C  
N  
Cu 2.03 ( 0.3)  
Ni 28.5 ( 2.3)  
Cd 6.38 ( 0.2)  
Fe 0.0227 ( 0.0019)  
Mn 8.7 ( 0.7)  
Zn  
Al  
Ba

MANOP S

GA225

type: 1  
volume: 5  
mass: 92

Ca  
P  
Si 0.0176  
C  
N  
Cu  
Ni  
Cd  
Fe  
Mn  
Zn  
Al  
Ba

MANOP S

X141

type: 3  
volume: 14.63  
mass: 230

Ca  
P 11.6  
Si  
C  
N  
Cu  
Ni  
Cd 71 ( 3)  
Fe 0.041 ( 0.008)  
Mn 10 ( 2)  
Zn  
Al  
Ba

MANOP S

X137

type: 3  
volume: 16.04  
mass: 230

Ca  
P 12.4  
Si  
C  
N  
Cu  
Ni  
Cd 81 ( 6)  
Fe 0.045 ( 0.008)  
Mn 11 ( 2)  
Zn  
Al  
Ba

MANOP S

X61

type: 3  
volume: 16.23  
mass: 230

Ca

P 0.014

Si

C

N

Cu

Ni

Cd 87 ( 5)

Fe 0.048 ( 0.008)

Mn 13 ( 2)

Zn

Al

Ba

MANOP S

X139

type: 3  
volume: 15.67  
mass: 230

Ca

P 0.004

Si

C

N

Cu

Ni

Cd 2.7 ( 0.4)

Fe 0.027 ( 0.008)

Mn 13 ( 3)

Zn

Al

Ba

MANOP S

X131

type: 3  
volume: 15.86  
mass: 230

Ca

P 0.0065

Si

C

N

Cu

Ni

Cd 3 ( 0.2)

Fe 0.063 ( 0.007)

Mn 4.9 ( 2.2)

Zn

Al

Ba

MANOP S

X109

type: 3  
volume: 15.78  
mass: 230

Ca

P 0.0039

Si

C

N

Cu

Ni

Cd 3.1 ( 0.2)

Fe 0.019 ( 0.008)

Mn 2.4 ( 1.5)

Zn

Al

Ba

BIOGRAPHICAL NOTE

The author was born on November 27, 1952, in Niskayuna, New York. He and his family lived in Schenectady and then Burnt Hills, New York, where he graduated from the Burnt Hills-Ballston Lake High School in 1970. From 1970-1974 he attended M.I.T. and graduated with an S.B. in Civil Engineering with a specialization in water resources. During these four years, he spent much of the time working and playing with the members of the M.I.T. Geochemistry Collective on the lakes, rivers, and estuaries of New England. He and Pat Mooney, also of Burnt Hills, New York, were married on July 27, 1974. The author entered Caltech in Pasadena, Ca. where he received an M.S. in Environmental Engineering and Science in June, 1975. While in Pasadena, he and his wife enjoyed the friendship of many people from Keck, the Athenaeum, and the Acapulco. In the spring of 1975, the author saved Russ McDuff's life - a favor which has since been returned many times over. In July, 1975, the author entered the MIT-WHOI Joint Program in Oceanography as a candidate for the degree of Doctor of Philosophy. Besides this thesis, the author has been involved with research in estuarine chemical processes, suspended particulate chemistry, and hydrothermal processes at the seafloor.

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