THE TRACE ELEMENT GEOCHEMISTRY OF MARINE BIOGENIC PARTICULATE MATTER

by

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SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

and the

WOODS HOLE OCEANOGRAPHIC INSTITUTION

November, 1980

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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

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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

transport of trace elements required to maintain their deep enrichment.

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

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

DEDICATION

To Pat and my parents

ACKNOWLEDGEMENTS

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

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

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

I am grateful to the brothers of Chi Phi, the people at the MIT Sailing Pavilion, and the Muddy Charles for being there when I needed them most.

Many sources of support must be mentioned. Although not directly contributing to this research, the MIT UROP and the NSF SOS programs supported the beginnings of my interest in the earth sciences. Portions of the data in this research have been collected under the NSF grant DES 75-03826 and ONR grant N00014-80-C-0273. I have been supported for the last three years on an NSF National Needs Graduate Traineeship to the MIT-WHOI Joint Program. Ship time was generously provided by various principal investigators of the NSF Galapagos Hydrothermal research program and the NSF-IDOE MANOP program.

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

My wife, Pat, has given me her love through these six years and made this thesis possible with her patience, her confidence in me, and her hard work as my graphic artist.

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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 developement 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 $CaCO_3$, opal, or $SrSO_4$; 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.

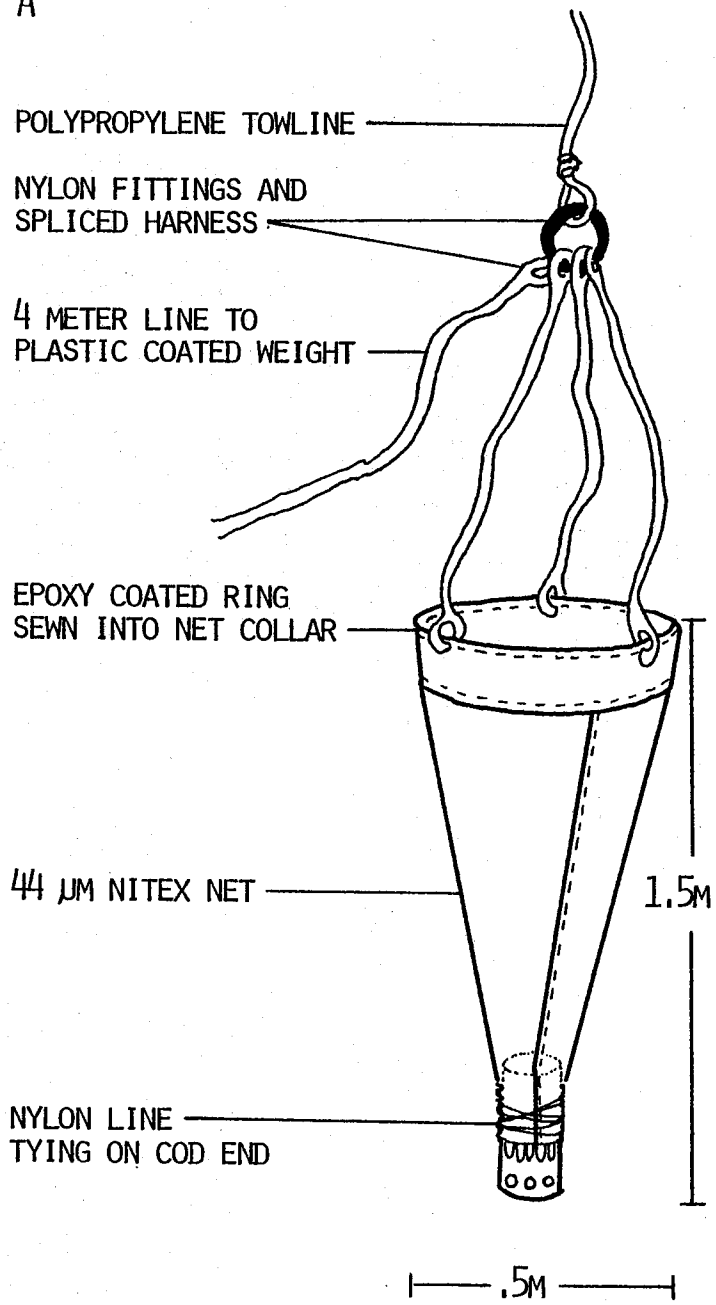
Throughout this research, one set of identical plankton nets was used (Fig. II-1a). These were conical, 3:1 in length-to-width ratio, with a 0.5 meter mouth, and made of 44μm Nitex nylon. The plankton were concentrated into two in-line, 1000 and 44μm Nitex bags contained in a PVC cod end, which was tied 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 polyproplene 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.

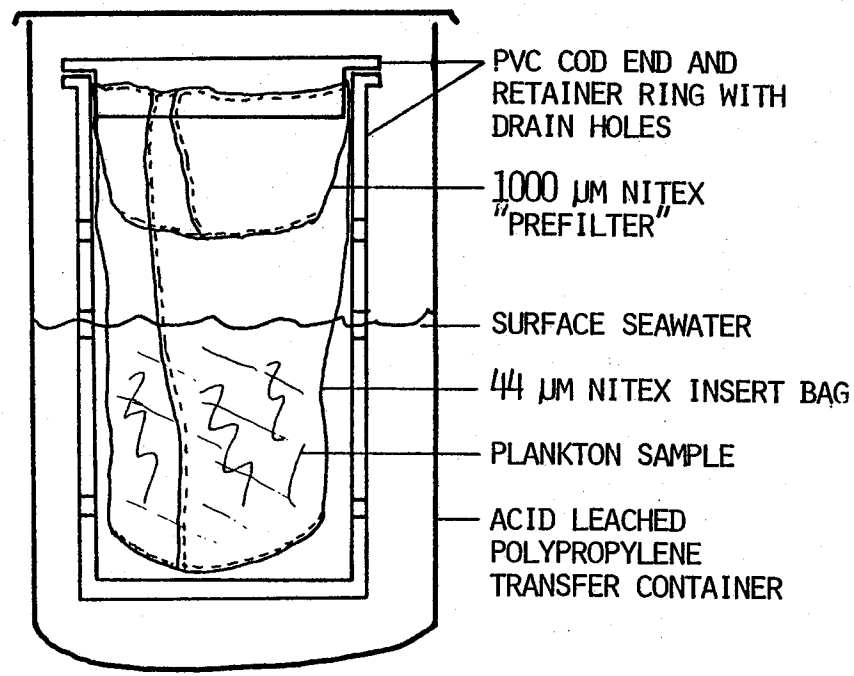
A) Net.

B) Cod end.

A


POLYPROPYLENE TOWLINE
NYLON FITTINGS AND SPLICED HARNESS
4 METER LINE TO PLASTIC COATED WEIGHT
EPOXY COATED RING SEWN INTO NET COLLAR
44 µM NITEX NET
1.5M
NYLON LINE TYING ON COD END
.5M

B


PVC COD END AND RETAINER RING WITH DRAIN HOLES
1000 µM NITEX "PREFILTER"
SURFACE SEAWATER
44 µM NITEX INSERT BAG
PLANKTON SAMPLE
ACID LEACHED POLYPROPYLENE TRANSFER CONTAINER

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 equiment 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^3 of seawater (not accounting for net clogging) and provided a sample of two to ten grams dry weight from productive surface waters.

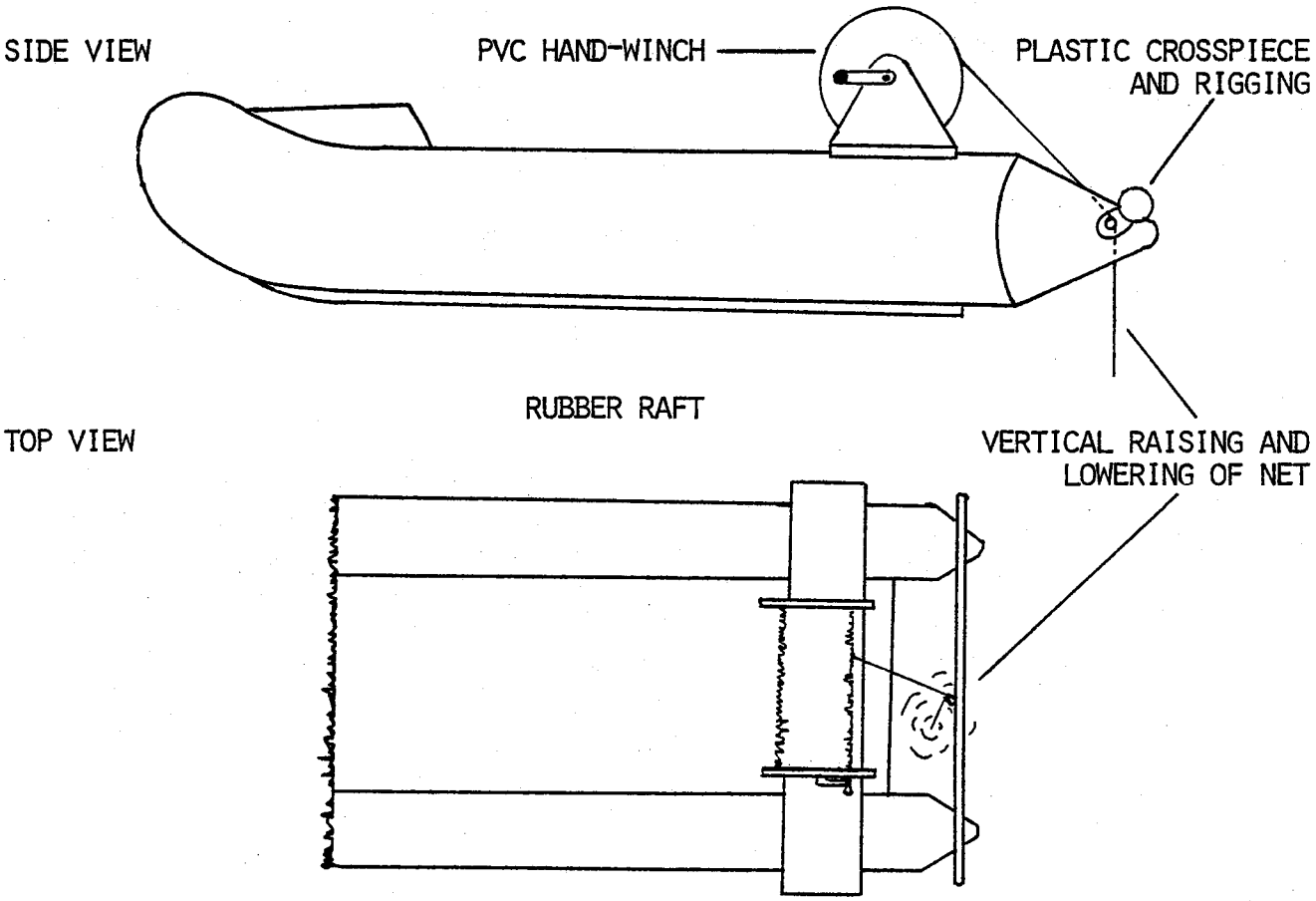
The hand-towing method, although far superior to normal ship tows in preventing contamination, was severely limited by wind, sea-state, and the low concentration of plankton found in the surface waters of oligotrophic environments. Therefore some plankton tows were collected from the main research vessel.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

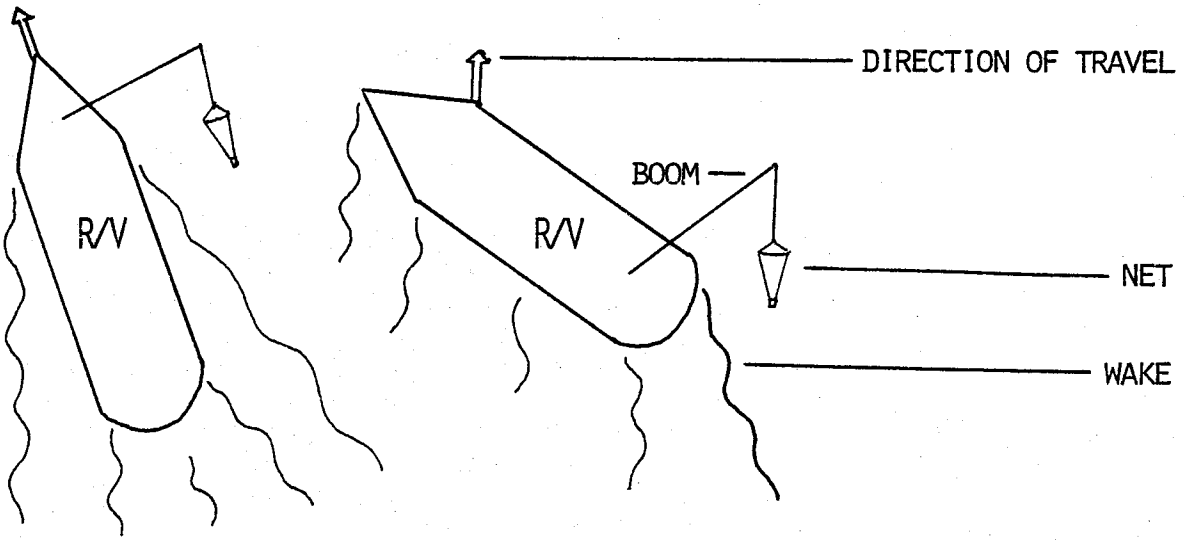
A) Zodiac rigging.

B) Ship and boom rigging.

A


SIDE VIEW
PVC HAND-WINCH
PLASTIC CROSSPIECE AND RIGGING
RUBBER RAFT
TOP VIEW
VERTICAL RAISING AND LOWERING OF NET

B


DIRECTION OF TRAVEL
BOOM
R/V
R/V
NET
WAKE

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 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 ($\pm$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 1.0μm 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