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Atmospheric Pathways of the Phosphorus Cycle

William F. Graham
University of Rhode Island

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ATMOSPHERIC PATHWAYS OF THE PHOSPHORUS CYCLE

BY

WILLIAM F. GRAHAM

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
OCEANOGRAPHY

UNIVERSITY OF RHODE ISLAND
1977

ABSTRACT

The flow of particulate phosphorus through the atmosphere has been studied. The goal of the work was to deduce the magnitude and direction of the fluxes of phosphours through the atmosphere and to identify the sources of this phosphorus. Samples of atmospheric particulate matter were collected at urban, rural, and remote continental sites, at remote island sites, and on ship-board over the Atlantic and Pacific Oceans. Samples of precipitation and dry fallout were collected at sampling sites at Narragansett, R.I. and Bermuda. Total phosphorus was determined on both the samples of atmospheric particulate matter and the deposition samples. In addition, the amounts of phosphorus considered to be "organic" and "reactive" were determined on the aerosol samples. Sodium, aluminum, and vanadium were also determined on the aerosol samples. These elements were used as tracers for the sea salt, crustal, and anthropogenic fossil fuel combustion portions of the aerosol.

The concentration of total particulate phosphorus in the atmosphere ranged from $\sim$100 ng m^{-3} in New York City to $\sim$0.2 ng m^{-3} at the geographic South Pole and down to $\sim$0.02 ng m^{-3} in the remote South Pacific. Typical concentrations in other areas were: Narragansett, R.I., 20 ng m^{-3}; Northwest Territories, Canada, 1.2 ng m^{-3}; the Western North Atlantic between North America and Bermuda, 7 ng m^{-3}; the North Atlantic near the coast of Northwest Africa, 70 ng m^{-3}; over the Peru current near the coast of Peru, 8 ng m^{-3}; and in the marine air near the islands of Hawaii and Samoa, 0.5 ng m^{-3}.

Particulate phosphorus in the marine air near Hawaii and Samoa came from both continental and oceanic sources. The reactive phosphorus fraction

was most closely associated with crustal material. An acid soluble inorganic fraction appears to have a marine source which could not be identified. The organic phosphorus fraction did not correlate with either aluminum or sodium. The material may have been derived from more than one source.

The particulate phosphorus found over the North Atlantic near the northwest coast of Africa appeared to come from the Sahara desert. Phosphorus to iron ratios in this aerosol agreed well with the ratios found in a desert soil from Libya. Much of the phosphorus in the marine air over the western North Atlantic appeared to be of anthropogenic origin. A strong correlation was found between phosphorus and vanadium, both in the reactive and organic phosphorus fractions. Much of the phosphorus in the nominally "organic" fraction was evidently a water insoluble organic form. The true amount of organic phosphorus could not be extracted from the North Atlantic aerosol data.

A field study in Narragansett Bay, R.I. using a bubble interfacial microlayer sampler showed that phosphorus is carried into the atmosphere on the drops from bursting bubbles and that it is enriched relative to sodium on these droplets. Enrichment of organic phosphorus ranged between 60-150, about ten times greater than that of reactive phosphorus. The source of this phosphorus appeared to be the sea-surface microlayer. The data from samples collected over the phosphorus-rich waters of the Peru current support the existence of the fractionation process in nature. A strong correlation was found between organic phosphorus and sodium in these samples. The average enrichment was 160.

The estimated global burden of particulate phosphorus in the atmosphere is 2.8 x 10^9g. The inputs of phosphorus to the atmosphere are estimated to be: crustal, $\sim 380 \times 10^{10}$ g y^{-1}, marine, $\sim 33 \times 10^{10}$ g y^{-1}, and anthropogenic, $\sim 46 \times 10^{10}$ g y^{-1}. Transport of crustal and anthropogenic material to the oceans is estimated to be $\sim 100 \times 10^{10}$ g y^{-1}, while transport of marine phosphorus to the continents is $\sim 3 \times 10^{10}$ g y^{-1}. These estimates are only good to a factor of two or three. An estimated $\sim 20 \times 10^{10}$ g y^{-1} of crustal phosphorus is readily released upon contact with ocean water. This amounts to about 10% of the riverine input of dissolved phosphorus to the oceans.

ACKNOWLEDGEMENTS

Many generous people and organizations have assisted me in the completion of this thesis. Contributions have included financial support, the loaning of equipment, the collecting of samples, or just being available to discuss ideas, problems, results, and future courses of action. The following is an attempts to thank all of them.

I thank, first and foremost, my wife, Marianna, for her willingness to bear the sacrifices and uncertainties of my midlife career change and for her unswerving encouragement and support. Besides buttressing me emotionally over these last five years, she has also materially improved this thesis by editing the entire manuscript.

Dr. Robert Duce, as my major professor, has given a great deal of time, thought, and effort in my support. At various times he has collected samples, provided generously of his supplies and equipment, edited proposals, listened to half-baked ideas with tolerance (if not amusement) and suggested directions for my research which have been fruitful and rewarding. One could not ask for more, I am proud to have been associated with him and to call him a friend.

My other committee members, Drs. Chris Brown and Michael Pilson, have provided valuable guidance to this thesis. Dr. Pilson has been especially generous in permitting me to use much of his laboratory equipment, and discussions of my problems with him were always stimulating and rewarding.

Many other faculty members, both at the Graduate School of Oceanography, and at the main University campus at Kingston have contributed to this work. Dr. James Fasching helped me over many a statistical problem, while Dr. George Felbeck greatly improved my understanding of soil chemistry. Drs. Michael Bender, Dana Kester, and James Quinn all discussed problems with me or allowed the use of laboratory facilities at one time or another.

My office mates were invaluable to me. Ms. Barbara Ray taught me the basics of air sampling techniques, helped me get my equipment where it was going on time, collected samples for me in Bermuda, and was always willing to discuss problems and possible solutions. Dr. Steven Piotrowicz shared his knowledge and library with me without reservation, along with a portion of every sample he collected in Narragansett Bay.

Other members of Dr. Duce's group were no less generous in time and effort. Dr. Kenneth Rahn, Mr. Randy Borys, and Mr. Paul Walsh, besides providing samples for me from the Northwest Territories and from New York City, were always willing to discuss aerosol chemistry with me. Dr. Rahn has also allowed me to use some of his data from the analysis of Sahara dust plume material. My thanks also to Dr. Ian Fletcher for collecting samples for me at Bermuda, Samoa, and the South Pole. Also to Mr. Cliff Weisel and Mr. Byard Mosher for their sample collection efforts at Samoa.

A special thanks to Dr. Eva Hoffman for her generous sharing of her organic carbon data with me and to Dr. Gerald Hoffman for all his help over the last five years.

Many persons outside of URI have also been very helpful to me. Dr. Lothar Schütz of the Max Planck Institute at Mainz provided me with portions of samples he collected in the Libyan desert and over the North Atlantic off the coast of Africa. My association with Dr. Schütz during his stay at URI has been most enjoyable.

I also wish to thank Dr. Fred Lepple of the NRL for his generous assistance. Dr. Lepple collected samples for me on a cruise of the HAYES in the Atlantic, shared samples collected on MIZAR cruise in the Pacific with me, and provided me with his data on the phosphorus content of Sahara dust. Thanks are also due to Dr. Philip Richardson of WHOI who allowed me to collect air samples on two of his TRIDENT cruises and to Dr. Terry Bidleman of the University of South Carolina who collected some samples for me on Barbados.

I deeply appreciate the support given to me by the National Science Foundation and the University of Rhode Island.

A special thanks to Ms. Cheryl Kornegay who waded quickly and efficiently through my illegible handwriting, converting it into the thesis before you.

And finally, to my children, Katie and David, without whose liberal application of apricot jelly to the kitchen table this thesis would have never stuck together.

PREFACE

This thesis has been prepared in manuscript form. It consists of drafts of five manuscripts. Introductory and concluding sections provide the background for the work and integrate the conclusions from the manuscripts. Two appendices discuss the analytical techniques used and provide a listing of the computer program used to calculate corrections for the activation analyses. The third appendix presents a listing of the samples collected at Narragansett, Rhode Island. A fourth appendix consists of a bibliography of all the literature cited in the thesis.

The first manuscript is entitled "Atmospheric input of phosphorus to remote tropical islands". It is to be submitted to the Journal of Ecology. This paper describes the concentrations of atmospheric phosphorus found in the marine atmosphere of Hawaii and American Samoa and discusses the possible sources of this material. The rate of deposition of phosphorus to these islands is estimated using these data.

The second manuscript is entitled "The transport of phosphorus to the North Atlantic by the Sahara dust plume". It is a brief paper in which the rate of transport of seawater soluble phosphorus from the African deserts to North Atlantic surface waters is estimated and compared to the rate of diffusive transport to these surface waters from the underlying deep waters. It is planned to submit this paper to the Journal of Geophysical Research.

The third manuscript is entitled "The atmospheric transport of phosphorus to the western North Atlantic". This manuscript reports the concentrations of phosphorus in the marine air over the western North Atlantic, discusses possible sources of this phosphorus, and estimates the input of phosphorus to the ocean surface in this region. This manuscript is to be submitted to Atmospheric Environment.

The fourth manuscript is titled "The sea as a source of atmospheric phosphorus". This manuscript is to be submitted to Marine Chemistry. The manuscript described the results of a study in Narragansett Bay on the injection of phosphorus to the atmosphere in the droplets from bursting bubbles and presents evidence for the occurrence of this process in nature.

The fifth manuscript is entitled "Atmospheric pathways of the phosphorus cycle". This manuscript is to be submitted to Geochimica Cosmochimica Acta. The paper brings together all the available information on the concentrations, sources, and deposition rates of phosphorus in the atmosphere, both from this research and from the literature. Using these data a global cycle of phosphorus in the atmosphere has been calculated and is presented in the manuscript.

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INTRODUCTION

> Les expériences faites sur l'eau de pluie et sur la neige, recueillies sur la tour de Pise à la hauteur de 54 mètres, avaient pour but la détermination des substances organiques et minérales, comme aussi la recherche de l'iode atmosphérique. Je n'ai pas réussi à constater la présence de l'iode dans ces eaux; seulement dans l'eau recueillie du 9 au 30 décembre j'ai obtenu, par un traitement convenable, une légere coloration rougeâtre qui probablement était due à la présence de l'iode; mais je dois ajouter que pendant les derniers fours de ce mois a soufflé un vent très-énergique qui a entraîné de la mer une quantité considérable de sel marin, et, en effet, l'eau en contenait une grande proportion.
>
> Les matières organiques qu'on a pu extraire de ces eaux et de la neige contiennent de 'lazote sous frome d'acide azotique et d'ammoniaque, c'est-à-dire que pour doser la totalité de l'azote de ces matières, le procédé à la chaux sodée n'est pas suffisant. Quelquefois ces mêmes matières, qu'on isole au moyen de traitements alcooliques, lorsqu'on les expose à la simple action de la chaleur, produisent une déflagration instantanee qui est due à une forte proportion d'azotate.
>
> Parmi les matières minérales, on y constate du chlorure de sodium en excès, de al chaux à l'état de carbonate, quelques traces de sulfates, etc., mais aucun indice n'indique la présence des phosphates.
>
> Au contraire, les résidus qu'on obtient par l'évaporation des eaux de pluie et de la neige recueillies à une petite distance du sol (3 à 4 metres) contiennent, outre les substances organizues, toutes les matieres qui se trovent dans la terre arable, et principalement les sels de chaux, de magnésie, d'alumine, la silice, les acides phosphorique, sulfurique, nitrique, le chlore et quelquefois l'iode.
>
> A une hauteur de 18 mètres du sol, les eaux et la neige contiennent encore le plus grant nombre des éléments de la terre arable et des matières organiques azotées; mais on n'y constate pas d'une maniere certaine les phosphates.
>
> de Luca (1861)

This early attempt to detect phosphorus in precipitation at Pisa, Italy was only partially successful. Phosphorus could not be found in a rain sample collected at the top of the Tower of Pisa, 54 m from the ground. At a height of 18 m, phosphorus could be seen occasionally. It was only in the sample collected at 3-4 m from ground level that phosphorus was strongly detected. The source of this phosphorus was considered to be soil.

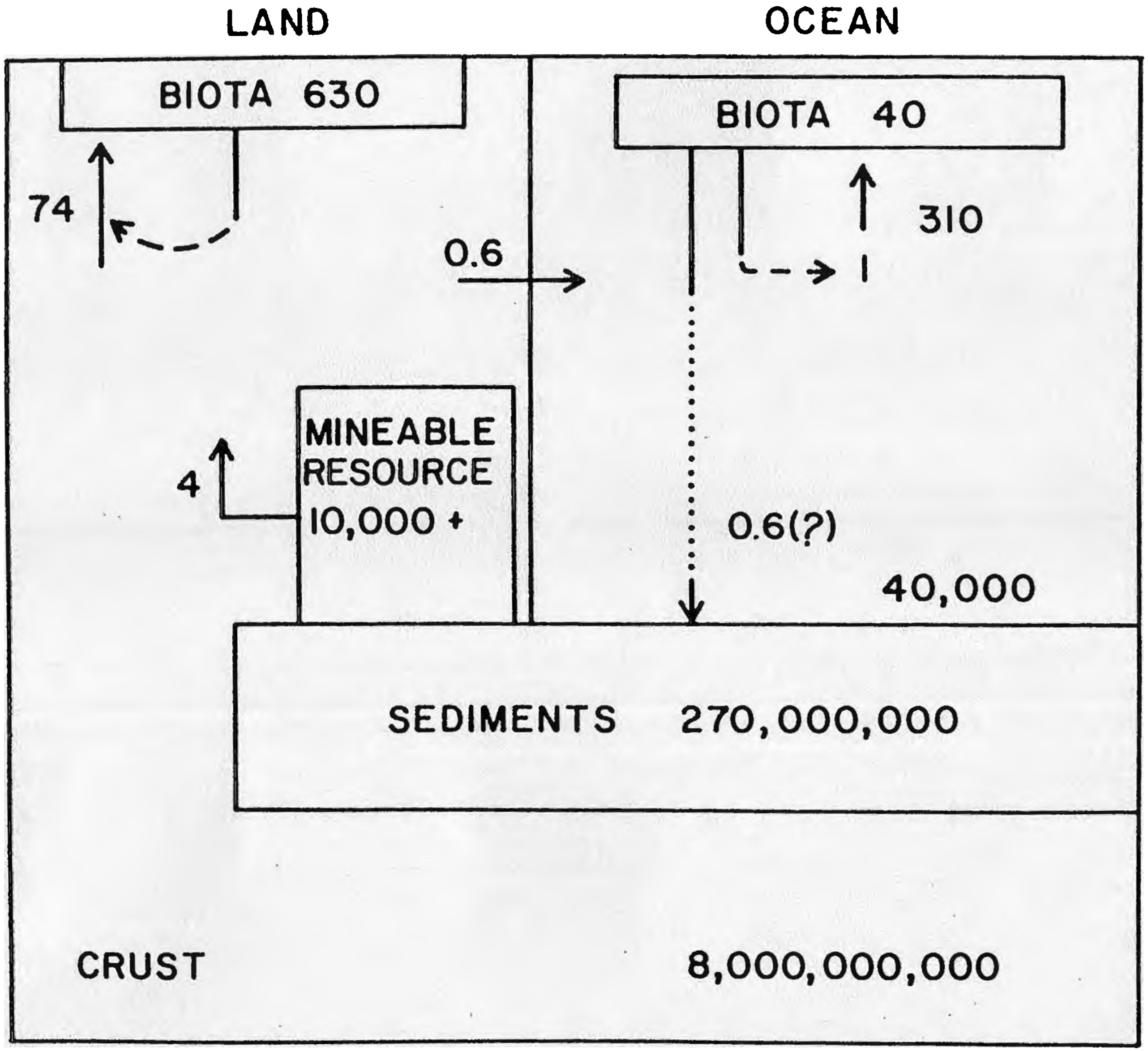
Other early accounts of the presence of phosphorus in precipitation are those of Trieschmann (1919) and Moore and Browning (1921), both reporting on the analysis of rain samples collected at Mt. Vernon, Iowa. From this period until the end of World War II no reports of phosphorus in the atmosphere or in precipitation have been found. A resurgence of interest occurred in the 1960's, when investigation into ecological and agricultural nutrient budgets led to several studies of phosphorus input through precipitation and dry fallout. Concerns over the quality of fresh waters have led to additional studies in recent years. Thus a fair body of data on the deposition of phosphorus in continental regions exists, and a few measurements of phosphorus concentrations in continental air, especially in urban regions, can be found. However, no data on phosphorus in the marine atmosphere were known to exist previous to the studies reported in this thesis, and the data that are available have never been integrated into a global view of phosphorus in the atmosphere.

The phosphorus cycle

Because phosphorus is a necessary element for all life, it is one of the most important minor constituents of the lithosphere. The flow of phosphorus from the lithosphere through the biosphere and hydrosphere has been illustrated qualitatively by Goldschmidt (1954). Broecker (1971) has discussed the interrelations of the phosphorus cycle to the cycles of other elements. According to Broecker (1971) the phosphorus and oxygen cycles are tied together by the need to balance phosphorus input to the oceans by the burial of phosphorus-containing organic matter in the sediments. According to this theory an increase in phosphorus input to the oceans would result in increased productivity in the surface waters. The increase in debris falling from the surface would result in a higher oxidative load in the deep water, with a subsequent enlargement of the anoxic areas of the ocean floor. As more phosphorus is buried in the sediments less would be released to the deep water and subsequently upwelled to the surface. Thus the oxygen and phosphorus contents of the deep water would reach a new equilibrium with the fluxes of phosphorus into and out of the oceans again in balance.

Interest in the phosphorus cycle and the possible consequences of perturbing it have led to several attempts to quantify the cycle. Emery et al. (1955) estimated the flux of dissolved and particulate phosphorus into the ocean via rivers along with the rate of phosphorus deposition in sediments. They concluded the two were roughly in balance. Stumm (1973) presented a much more detailed cycle (Fig. 1). Broecker (1974) suggests that while man's current additional input of phosphorus to the oceans will have little effect on total oceanic plant production, transient effects in rivers and estuaries could be quite large. Stumm (1973) points out that the application of phosphate fertilizers has increased tenfold over the last fifty years and that a similar rate of increase might be expected in the future. Because a rapid increase in the phosphorus input to the oceans may occur over decades while the regulatory response may be 100-1000 times slower, undesirable changes in plant and animal life may occur, especially in coastal waters. Under anoxic conditions the higher forms of life are

Fig. 1 The phosphorus cycle of Stumm (1973). Reservoirs are in units of 10^{10} mols, fluxes in units of 10^{10} mols y^{-1}.


LAND
OCEAN
BIOTA 630
BIOTA 40
74
310
0.6
MINEABLE RESOURCE 10,000 +
4
0.6(?)
40,000
SEDIMENTS 270,000,000
CRUST
8,000,000,000

eliminated completely (Stumm, 1973).

Another cycle has been calculated by Lerman et al. (1975) (Fig. 2). This cycle is a little more complete than Stumm's (Stumm, 1973) as it includes both dissolved and particulate phosphorus fluxes to the ocean. Lerman et al. (1975) calculate that, if the input of phosphorus to the oceans increases at the same rate as the agricultural application of phosphorus to land, in sixty years the mineable reservoirs are depleted, the ocean phosphorus content has increased by 38 percent, and the amount of oceanic biota has increased by 30 percent. Under these conditions, severe changes in composition of the oceanic biota would be expected.

The extrapolations of anthropogenic phosphorus input to the oceans by Stumm (1973) and Lerman et al. (1975) were made before the current energy crisis. The higher energy cost of fertilizer production may greatly reduce the actual rates of increase of phosphorus to the oceans.

The most recent cycle is that of Pierrou (1976) (Fig. 3). Unlike the others, Pierrou makes no attempt to balance his cycle. The cycle is of particular interest because it is the only one that includes a freshwater segment and the only one that contains any estimates of atmospheric phosphorus fluxes. However, Pierrou's estimates are based on extremely limited data, and Pierrou himself states:

> The atmospheric part of the phosphorus cycle seems to be poorly known...it appears that dust from terrestrial areas and sea spray are the major sources of phosphorus in the atmosphere. Unfortunately no measurements or estimates seem to have been published on this subject.

The purpose of the research described in the manuscripts of this thesis is to fill this gap in the phosphorus cycle.

Fig. 2 The phosphorus cycle of Lerman et al. (1975). Reservoirs are in units of 10^{12} g, fluxes in units of 10^{12} g y^{-1}.

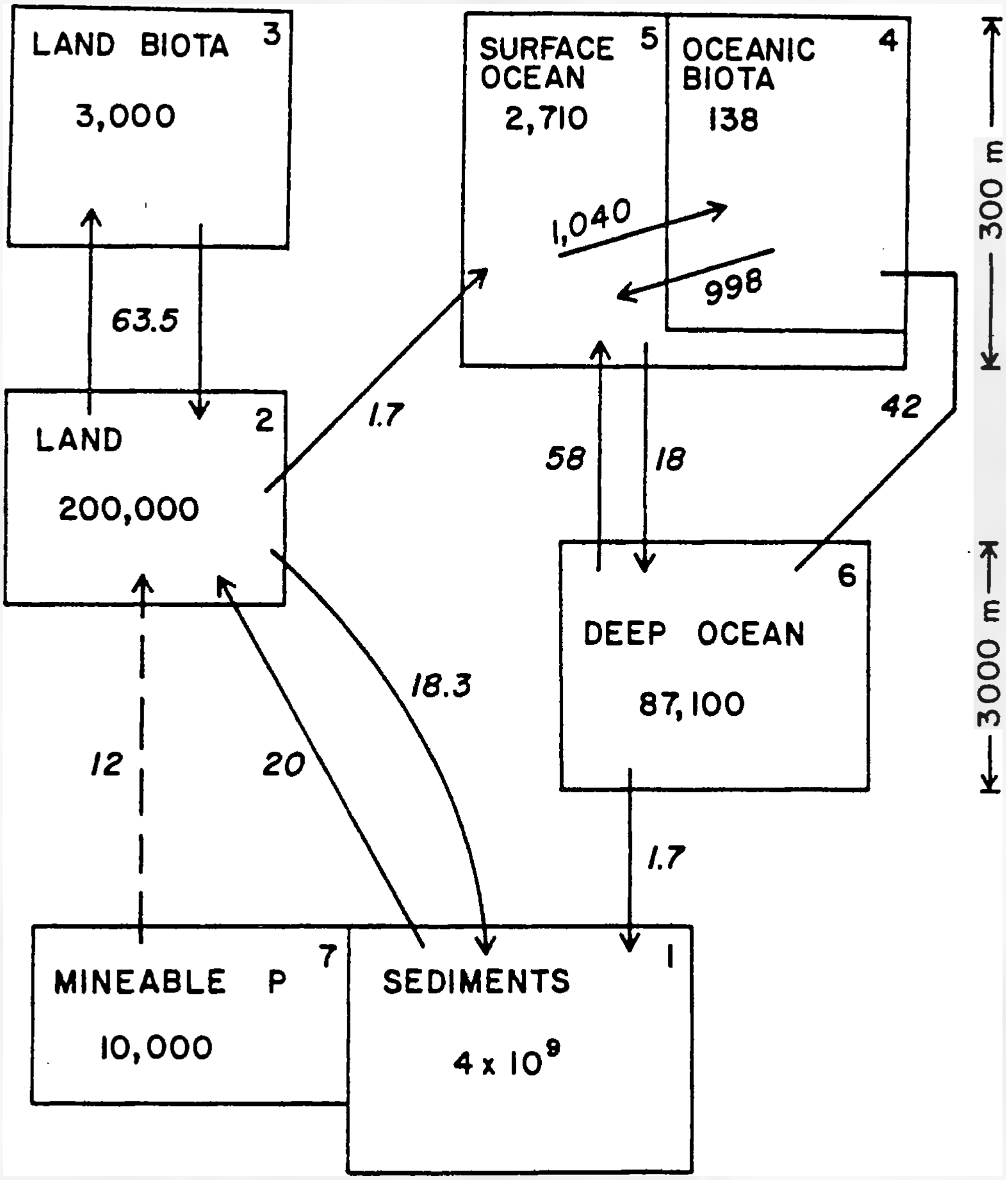
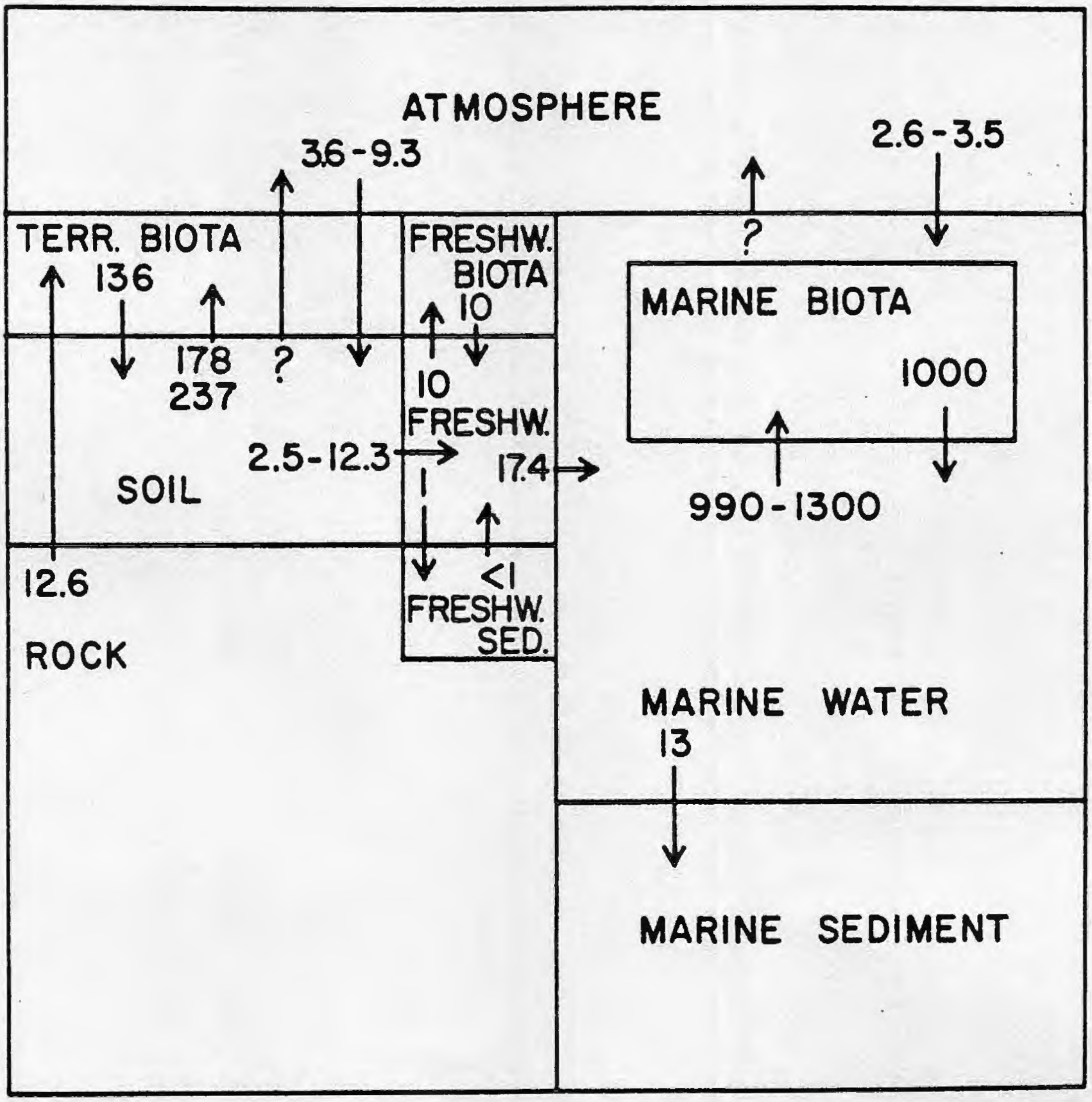

LAND BIOTA
3
3,000
63.5
LAND
2
200,000
1.7
SURFACE OCEAN
5
2,710
OCEANIC BIOTA
4
138
1,040
998
300 m
58
18
42
DEEP OCEAN
6
87,100
3000 m
18.3
12
20
1.7
MINEABLE P
7
10,000
SEDIMENTS
1
4 x 10⁹

Fig. 3 The phosphorus cycle of Pierrou (1976). Reservoirs are in units of 10^{12}g, fluxes in units of 10^{12} g y^{-1}.


ATMOSPHERE
3.6 - 9.3
2.6 - 3.5
?
TERR. BIOTA
136
178
237
?
FRESHW. BIOTA
10
10
FRESHW.
2.5-12.3
17.4
1
<1
FRESHW. SED.
SOIL
12.6
ROCK
MARINE BIOTA
1000
990-1300
MARINE WATER
13
MARINE SEDIMENT

ATMOSPHERIC INPUT OF PHOSPHORUS TO REMOTE TROPICAL ISLANDS

ABSTRACT

Atmospheric particulate phosphorus has been measured in the trade winds of the Hawaiian and Samoan islands. The concentration of phosphorus ranges from 300-800 pg m^{-3} and averages about 500 pg m^{-3}. Reactive phosphorus comprises 20 to 35% of the total phosphorus, persulfate releasable phosphorus 20-35%, and acid soluble phosphorus 40-60%. The reactive phosphorus appears to be of crustal origin, while the acid soluble fraction is of marine origin. The origin of the persulfate releasable phosphorus is not readily apparent. The acid soluble fraction may be either organic or inorganic in nature. The persulfate releasable fraction appears to be comprised of organic material. The net phosphorus input to the vegetation on the windward sides of these islands is estimated to be 0.025 - 0.030 Kg ha y^{-1}. The value amounts to 15-20% of the phosphorus deposition measured at an island site. It appears that bulk precipitation samples are easily contaminated in regions of intense biological activity.

INTRODUCTION

The input of phosphorus compounds from the atmosphere to forests, croplands, and inland water bodies has been widely measured in temperate zones as part of ecological and water quality studies. However, data from tropical regions are much fewer. The most comprehensive study appears to be that of Ungemach (1972) at Manaus, Brazil in the Amazon Basin. Other measurements of phosphorus input from the atmosphere in tropical regions have been made in Ghana (Nye, 1961), Nigeria (Jones, 1960), The Gambia (Thorton, 1965), and the Kerala coast of India (Vigayalakshmi and Pandalai, 1963). Phosphorus inputs reported by these investigations range from 0.14 to 4.3 Kg $ha^{-1}y^{-1}$.

Almost no data are available on the flux and sources of atmospheric phosphorus to the vegetation of islands. An Antarctic island has been studied by Allen et al. (1967). Based on Allen's analysis of rain water, one calculates that precipitation on this island, located in the midst of phosphate rich Antarctic waters, contributed about 0.15 Kg $ha^{-1}y^{-1}$ of phosphorus to the island's vegetation. In a study of mineral cycles in the El Verde Forest of Puerto Rico, Jordan and Drewry (1969) report an input of phosphorus in rain of 1.81 Kg $ha^{-1}wk^{-1}$. This is the equivalent of 94 Kg $ha^{-1}y^{-1}$ and seems to be high compared to the other data.

Many major Pacific tropical islands are of volcanic origin. Soils of these islands are often acidic, have relatively high contents of amorphous ferric and aluminum oxides, and consequently have a very high fixation capacity for phosphorus (Fox et al., 1968; Younge and Plucknett, 1966). Because of the strong fixation capacity of these soils, losses of available phosphorus in leaching and runoff should be very low. However, some loss most assuredly does occur. Natural sources of phosphorus which replace this loss would appear to be weathering and input from the atmosphere. Estimating the magnitude of the atmospheric input is the concern of this paper.

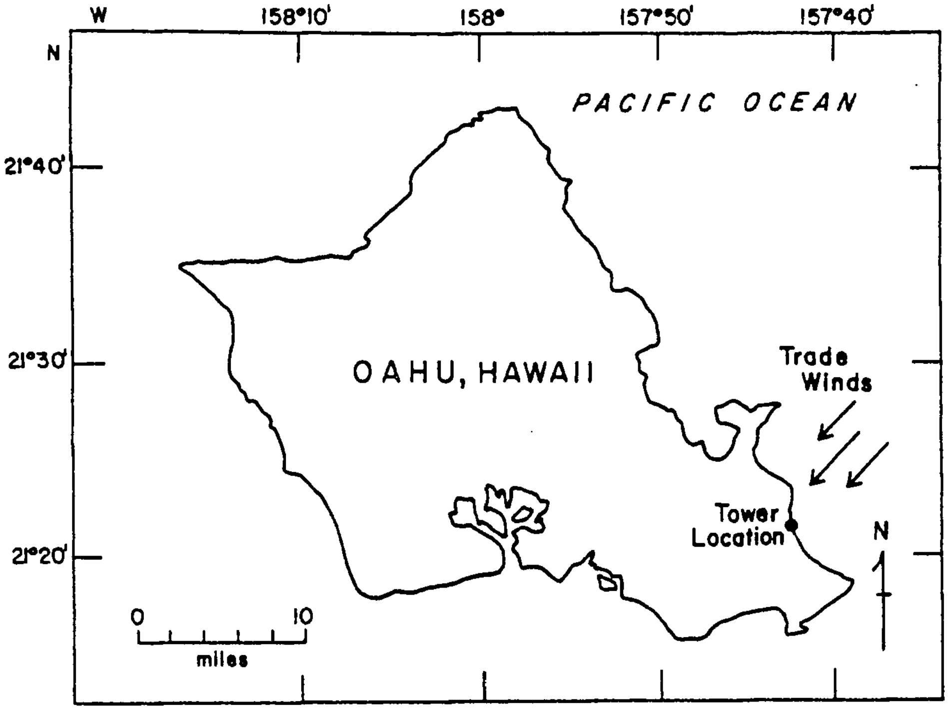
SAMPLING SITES

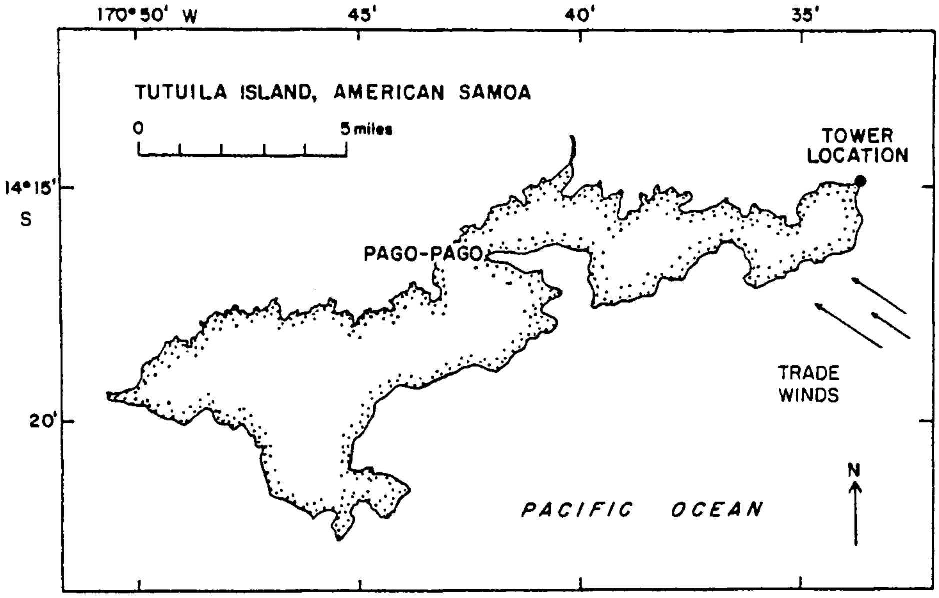
My study of atmospheric input of phosphorus was carried out at sampling stations at Bellows AFS, on the island of Oahu, Hawaii, and at the NOAA GMCC station at Cape Matatula, Tutuila Island, American Samoa. Both locations are on the windward sides of the respective island in locations that provide maximum exposure to the onshore winds from the prevailing trade winds (Fig. 1).

SAMPLING METHODS

Samples of atmospheric particulate matter were collected from the top of 20 meter towers situated at each site. The samples were collected with Cadillac sampling pumps connected to 20 x 25 cm polystyrene filters (Delbag Microsorban 97/99). Delbag filters are reported to be 99% efficient in the removal of particles >0.3 μm in diameter (Dams et al., 1972). The time of sampling ranged from three to seven days, during which 5000 to 14,000 m^3 of air passed through the filters. Due to the persistence of the northeast trades at Hawaii during the sampling period (August to October 1975), samples were collected continuously. At American Samoa, where the winds were more variable over a longer sampling period, the sampling pumps were connected to an automatic control system which shut

Fig. 1 Sampling sites on the islands of Oahu, Hawaii and Tutuila, American Samoa.


W
158°10'
158°
157°50'
157°40'
N
21°40'
21°30'
21°20'
PACIFIC OCEAN
OAHU, HAWAII
Trade Winds
Tower Location
N
0
10
miles


170°50' W
45'
40'
35'
14°15' S
20'
TUTUILA ISLAND, AMERICAN SAMOA
0
5 miles
TOWER LOCATION
PAGO-PAGO
TRADE WINDS
PACIFIC OCEAN
N

down sampling during periods of non-marine winds, calm, rain, or high counts of Aitken nuclei. The sampling system has been described in detail by Duce et al., (1976). A size separated aerosol sample for phosphorus analysis was collected at the Hawaii site with a Sierra Model 235 high volume cascade impactor. Delbag collection strips and backup filters were used. According to the manufacturer, the equivalent aerodynamic radius cutoffs at 50% collection efficiency for particles with a density of 1 g cc^{-1} are as follows: Stage 1 = 3.6 μm; Stage 2 = 1.5 μm; Stage 3 = 0.75 μm; Stage 4 = 0.48 μm; Stage 5 = 0.25 μm; final filter = $\leq$0.25 μm. The impactor sample was collected over a seven-day period.

In addition to samples of atmospheric particulates, bulk precipitation samples were collected at Samoa on the roof of the NOAA laboratory. A 0.36 m^2 rain sampling funnel was connected to a 20 l polyethylene jerrycan. The funnel was covered with polyethylene screening to exclude insects and large particles. The jerrycan was emptied into one-liter glass bottles after each rain. Forty mg/l of Hg_2Cl_2 were added to each precipitation sample as a preservative. All filter and precipitation samples were shipped to the University of Rhode Island for analysis.

CHEMICAL ANALYSIS

Each filter sample was divided into four quarters for analysis. Two quarters were pelleted individually and then analyzed separately for sodium and aluminum by neutron activation analysis. The pellets were irradiated for 30 seconds in the Rhode Island Nuclear Science Center swimming pool reactor at a flux of $4 \times 10^{12} n\ cm^{-2} s^{-1}$. Within two minutes the samples were counted for 400s on a Ge(Li) detector (resolution of 2.3 KeV for the 1,332 KeV gamma ray of ^{60}Co) coupled to a Nuclear Data 2200 4096 channel analyzer with a computer-compatible magnetic tape output (Ampex TM-7) for spectrum analysis. A computer program (J.L. Fasching, personal communication) was used to process the Ge(Li) spectra acquired. Absolute standards for sodium and aluminum were prepared on blank filters, pelleted, irradiated and counted in the same manner as the unknowns. Constant geometry was maintained during the counting of all standards and unknowns. Corrections were made for dead time and half-life discrimination.

After decay of any residual radioactivity, these quarters were ashed at 550°C in the presence of excess magnesium. The residues were dissolved in 1 ml of 1 N HCl, diluted to 40 ml and filtered. Any arsenate present was reduced to arsenite by the method of Johnson and Pilson (1972). Phosphorus was determined using the ascorbic acid method of Murphy and Riley (1962). Phosphorus determined in this manner is called "total phosphorus".

The recovery of commercially available iron and calcium phosphates using this technique was 100%. Only 50% of a commercial aluminum phosphage was recovered. The degree of recovery of more complex phosphorus minerals is unknown.

One quarter of the filter sample was extracted with agitation for thirty minutes using doubly distilled water. After filtration and arsenate reduction, the phosphorus present was determined colorimetrically as above. Phosphorus determined on this portion of the filter is called "reactive".

The last quarter was treated with 5 ml of 6.4% potassium persulfate solution in 40 ml of double distilled water, and autoclaved for 25 mintutes at 125°C (Menzel and Corwin, 1965). After filtration, the solution was analyzed for phosphorus as above. Due to interference by the oxidizing agent, arsenate was not reduced in this analysis. However, much of the arsenate is probably lost in the autoclaving step. In any case, the error introduced is small, as total atmospheric aesenic compounds found at these sites is only about 4% of the phosphorus (Walsh, personal communication). Phosphorus determined by persulfate oxidation includes reactive phosphorus, phosphorus that is liberated during the oxidation of organic material, and inorganic phosphorus which is soluble at the final pH of the oxidation reaction (pH ≈2). Studies with a variety of organophosphorus compounds showed that the efficiency of oxidation ranged between 85 and 100% for most organophosphorus compounds. However, the recovery of phosphorus from phytic acid (inositol hexaphosphate) was very low, averaging 10%. The phosphorus determined in this analytical step is called "total persulfate phosphorus".

The "persulfate releasable" phosphorus fraction is the difference between the total available phosphorus and the reactive phosphorus. A fraction called "acid soluble" is defined as the difference between the total phosphorus value and the total available phosphorus value.

Analytical precisions in the atmospheric samples have been calculated to be: total P, ± 10%; total available P, ± 15%; reactive P, ± 20%; sodium, ± 9%; aluminum, ± 16%.

Only total persulfate phosphorus was determined on the precipitation samples using the persulfate oxidation technique after filtration in the laboratory. Because the samples could not be analyzed immediately after collection, meaningful values for reactive phosphorus could not be obtained. The analytical precision in the measurement of phosphorus in precipitation was about ± 4%.

RESULTS AND DISCUSSION

In Tables 1 and 2 I present the analytical results on the filter samples along with the pertinent meteorological data. Table 3 summarizes these concentrations and gives the distribution of the different phosphorus fractions. In the dry season, about the same amount of phosphorus was found in the marine air of Hawaii and Samoa; the major difference is that the reactive phosphorus level in Samoan air was about one-half that of Hawaiian air. Soluble and organic phosphorus levels were similar at the two sites. The major difference between wet and dry season samples in Samoa was the lower level of organic phosphorus during the wet season. Acid soluble and reactive phosphorus did not appear to be greatly affected by the change in seasons.

Figure 2 illustrates the distribution of phosphorus, sodium, and aluminum on a cascade impactor sample taken in Hawaii. Due to the low levels of phosphorus on each stage, only total phosphorus could be determined. For comparison, the figure also shows the size distribution of total organic carbon in Hawaiian air as determined by Hoffman and Duce (1977). For the larger size particles, the phosphorus distribution matched fairly well that of sodium. In the finer fractions, the behavior is more complex and subject to some uncertainty in interpretation.

The analysis of the bulk precipitation samples are shown in Table 4. The total available phosphorus content in the precipitation samples ranged from 2 to 145 μg/l. However, input rates on a unit time basis proved to be more constant, ranging from 0.09 to 0.90 mg $ha^{-1}day^{-1}$. The annual input of total available phosphorus is estimated to be 0.14 Kg $ha^{-1}yr^{-1}$.

Sources of phosphorus in the atmosphere

TABLE 1. Meteorological conditions and concentration of phosphorus in samples of atmospheric particulate matter from the marine air of Hawaii

LOCATION	SAMPLE	1975 DATE	AVG. WIND VELOCITY m/s	PERCENT "GOOD" WINDS	PRECIP. cm	PHOSPHORUS - pg m^{3}					SODIUM µg m^{-3}	ALUMINUM ng m^{-3}
						TOTAL	TOTAL AVAIL.	REACTIVE	PERSULFATE RELEASABLE	ACID SOLUBLE		
Hawaii (August - October, 1975)	1	11 Aug	7.1	100	0.03	500	460	90	370	40	2.5	11
	2	14 Aug	10.0	100	0.13	860	370	300	70	490	4.3	22
	3	18 Aug	8.1	100	0.03	480	380	160	220	100	3.2	8
	4	22 Aug	8.4	100	0.20	470	250	60	190	220	3.8	20
	5	28 Aug	6.6	95	0.46	420	220	150	70	200	2.2	18
	6	3 Sep	8.0	99	0.03	500	220	110	110	280	3.6	11
	7	8 Sep	8.1	100	0.28	390	170	110	60	220	2.9	7
	8	12 Sep	5.4	76	0.10	430	320	190	130	110	1.6	11
	9	18 Sep	8.4	100	0.03	770	550	450	100	220	2.9	21
	10	24 Sep	7.6	100	0.03	530	350	140	210	180	3.0	13
	11	30 Sep	7.2	98	0.20	440	270	220	50	170	2.6	14
	12	6 Oct	9.1	100	0.71	380	170	70	100	210	3.5	4
	13	12 Oct	7.9	98	0.03	260	130	70	60	130	2.5	5
	Mean		7.8	97	0.17	490	300	170	130	200	3.0	13
	±S.D.		±1.1		±.21	±160	±120	±110	±90	±110	±0.7	±6

TABLE 2. Meteorological conditions and concentrations of phosphorus in samples of atmospheric particulate matter from the marine air of American Samoa

						PHOSPHORUS - pg m^{-3}						
LOCATION	SAMPLE	1976 DATE	AVG. WIND VELOCITY m/s	PERCENT "GOOD" WINDS	PRECIP. cm	TOTAL	TOTAL AVAIL.	REACTIVE	PERSULFATE RELEASABLE	ACID SOLUBLE	SODIUM µg m^{-3}	ALUMINUM ng m^{-3}
Samoa (January-February, 1976)	1	11 January	5.8	80	11.53	400	190	60	130	220	2.7	3
	2	18 January	6.8	85	13.38	425	180	130	50	240	3.2	8
	3	25 January	4.2	96	1.37	330	180	100	80	150	2.3	17
	4	1 February	3.9	86	1.42	320	100	70	30	220	1.8	3
	5	5 February	4.1	73	3.84	560	140	80	60	430	2.5	1
	MEAN		5.0	84	6.34	410	160	90	70	250	2.5	6
	± S.D.		±1.3		±5.77	±100	±40	±30	±40	±100	±0.5	±6
Samoa (June - September, 1976)	1	16 June	5.9	94	2.80	510	380	40	340	140	3.4	5
	2	25 June	5.0	86	2.84	590	520	160	360	60	2.9	2
	3	2 July	10.4	87	1.57	510	170	60	110	360	3.7	5
	4	9 July	5.9	95	5.03	400	130	20	110	270	3.9	2
	5	16 July	6.9	48	3.96	800	200	N.D.	200	600	2.4	13
	6	23 July	8.6	80	2.82	340	100	50	50	230	2.7	8
	7	1 August	7.0	80	-	440	150	120	30	290	3.1	7
	8	8 August	7.1	56	2.64	650	160	N.D.	160	490	2.6	4
	9	15 August	12.7	73	0.38	500	140	N.D.	140	400	3.9	14
	10	22 August	5.3	92	0.28	620	220	120	100	390	6.2	8
	11	28 August	8.9	100	0.25	450	170	20	150	280	3.5	8
	12	4 September	4.5	100	0.01	320	140	40	100	190	4.8	6
	13	11 September	5.6	86	0.07	410	270	200	70	130	2.3	7
	14	18 September	4.9	58	3.10	430	180	170	10	240	1.6	7
	MEAN					500	210	70	140	290	3.4	6
	± S.D.					±130	±110	±70	±100	±150	±1.1	±4

Table 3. The concentrations and distribution of atmospheric particulate phosphorus compounds in the marine air of Hawaii and Samoa.

	HAWAII		SAMOA[1]			
	DRY SEASON[8]		RAINY SEASON[6]		DRY SEASON[7]	
FRACTION	pg m^{-3}	%	pg m^{-3}	%	pg m^{-3}	%
Total P	500	100	370[2]	100	470	100
Total Persulfate P	290	58	160[3]	43	240	51
Reactive P	160[4]	34	90	24	90	19
Persulfate Rel. P	130	26	70[5]	19	150	32
Acid Sol. P	210	42	210	57	230	49

[1] Excludes all samples with less than 80% "good" winds

[2] Significantly less than other values at 92% c.l.

[3] Significantly less than other values at 93% c.l.

[4] Significantly higher than other values at 98% c.l.

[5] Significantly less than other values at 90% c.l.

[6] December - February, 1976

[7] June - September, 1976

[8] July - October, 1976

Fig. 2 The concentration of total phosphorus, sodium, aluminum, and total organic carbon as a function of cascade impactor stage. Largest particles on stage 1, smallest on stage 5. F = backup filter.

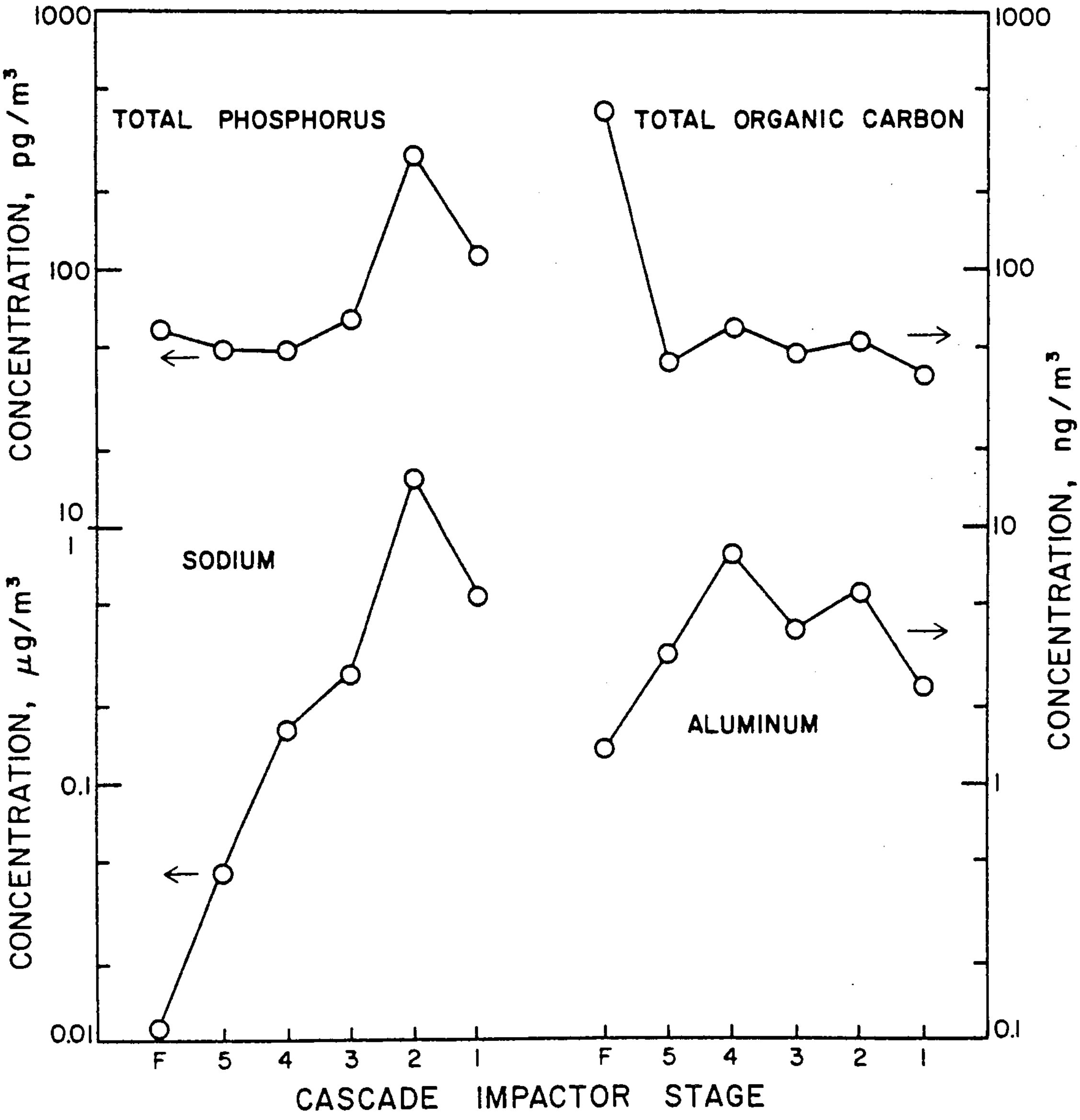

TOTAL PHOSPHORUS
TOTAL ORGANIC CARBON
SODIUM
ALUMINUM
CONCENTRATION, pg/m³
CONCENTRATION, μg/m³
CONCENTRATION, ng/m³
1000
100
10
1
0.1
0.01
1000
100
10
1
0.1
F
5
4
3
2
1
F
5
4
3
2
1
CASCADE IMPACTOR STAGE

TABLE 4. The input of phosphorus in bulk precipitation at Samoa

SAMPLE	DATE ON	DAYS EXPOSED	PPTN cm	TOTAL AVAILABLE P IN PPTN $\mu g\ l^{-1}$	TOTAL AVAILABLE P AS BULK DEPOSITION $mg\ ha^{-1} day^{-1}$
1	10 Dec 75	6	10.64	3.1	0.55
2	16 Dec 75	17	8.33	10.4	0.51
3	2 Jan 76	6	10.62	3.2	0.55
4	8 Jan 76	5	2.87	4.0	0.22
5	13 Jan 76	4	6.93	1.9	0.33
6	17 Jan 76	3	6.48	2.7	0.57
7	20 Jan 76	17	4.37	11.9	0.30
8	6 Feb 76	8	8.81	3.5	0.39
9	14 Feb 76	5	2.82	3.7	0.21
10	25 Jun 76	1	0.78	4.6	0.36
11	26 Jun 76	2	0.83	5.5	0.23
12	28 Jun 76	1	1.19	4.8	0.56
13	29 Jun 76	3	0.03	145	0.12
14	2 Jul 76	1	0.20	52	0.95
15	3 Jul 76	1	0.03	99	0.25
16	4 Jul 76	2	0.13	58	0.38
17	6 Jul 76	1	0.25	31	0.74
18	9 Jul 76	3	0.18	38	0.23
19	12 Jul 76	1	1.47	6.2	0.97
20	13 Jul 76	1	1.21	3.7	0.39
21	14 Jul 76	4	2.03	5.2	0.24
22	18 Jul 76	1	0.84	3.7	0.32
23	19 Jul 76	1	0.71	5.6	0.40
24	20 Jul 76	2	0.28	6.5	0.09
25	22 Jul 76	1	0.30	9.9	0.31
26	23 Jul 76	2	0.36	12	0.21
27	25 Jul 76	2	1.14	3.0	0.17
28	27 Jul 76	1	0.70	13	0.95
29	28 Jul 76	1	1.52	4.0	0.61

Total Days = 103

Total Input of Available Phosphorus = 40.1 g ha^{-1}

Estimated Annual Input = 0.14 kg $ha^{-1}y^{-1}$

Data matrices consisting of the various phosphorus fraction concentrations along with the concentrations of aluminum and sodium were analyzed by factor analysis and by multi-variate linear regression. Factor analysis is a statistical technique for the grouping of linear combinations of similar variances from variables that are highly correlated. The theory of factor analysis has been presented in detail by Harman (1967). The application of factor analysis to the measurements of trace elements in the atmosphere have been described by Hopke et al (1976) and Duce et al. (1976).

The results of the factor analysis of the experimental data are presented in Table 5. Using an eigenvalue cutoff of 1, three factors were found to account for 87% of the variation of the Hawaiian data, 86% of the Samoan data, and 89% of the pooled data.

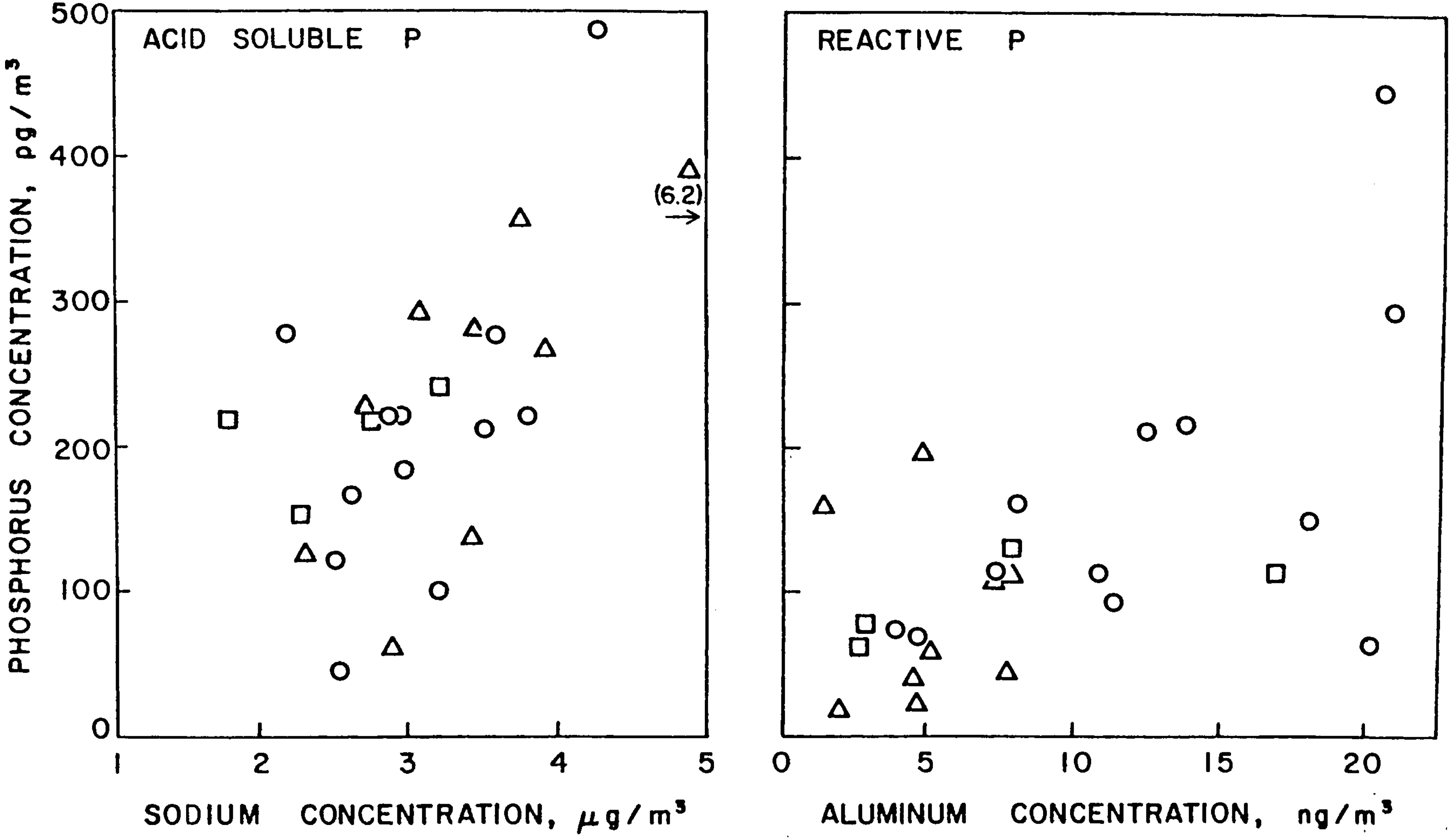
The first factor contains most of the sodium variation and most certainly represents sea salt particles ejected from the ocean by bubble action. Sodium concentration correlates with the square of the wind velocity (r = 0.35, sig. = 0.95) as would be expected from the work of Woodcock (1953) and Blanchard (1963).

Most of the acid soluble phosphorus variation also appears in factor 1, indicating that the ocean is the most likely source for this phosphorus fraction. Fig. 3 shows that the concentration of acid soluble phosphorus in marine air at these sites increases as the sodium concentration increases. The type of phosphate that comprises this fraction is not obvious. One possibility is the presence of organic phosphates which are resistant to persulfate oxidation. This would imply that only 30-50% of the organic matter present on the filters was oxidized by the persulfate method. Inositol phosphates are one possible source of this persulfate resistant

TABLE 5. Results from factor analysis performed on the data matrix from the Hawaiian and Samoan sample sets.

	HAWAII			SAMOA			COMBINED DATA		
	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 1	FACTOR 2	FACTOR 3
Eigenvalues	2.84	1.37	0.99	1.91	1.30	0.91	1.95	1.48	1.02
Portion	0.47	0.23	0.17	0.38	0.30	0.18	0.39	0.30	0.20
Cum. Portion	0.47	0.70	0.87	0.38	0.68	0.86	0.39	0.69	0.89
Variance									
Reactive P	-0.097	0.891	-0.216	-0.125	-0.905	-0.027	-0.066	-0.898	-0.041
Persulf. Rel. P	-0.149	-0.074	0.969	0.002	0.116	0.934	0.023	0.069	0.979
Acid. Sol. P	0.714	0.440	-0.393	0.769	-0.391	-0.453	0.761	-0.137	-0.566
Sodium	0.926	0.054	0.083	0.982	0.126	0.141	0.963	0.037	0.110
Aluminum	0.309	0.874	0.117	0.044	0.454	0.675	0.108	-0.891	-0.086

Fig. 3 Left: the concentration of acid soluable phosphorus vs. the concentration of sodium in marine air at Hawaii and Samoa. Right: the concentration of reactive phosphorus vs. aluminum at the same sites. ○ - Hawaii, □ - Samoa, rainy season, △ - Samoa, dry season.


ACID SOLUBLE P
REACTIVE P
PHOSPHORUS CONCENTRATION, pg/m³
500
400
300
200
100
0
(6.2)
1
2
3
4
5
SODIUM CONCENTRATION, μg/m³
0
5
10
15
20
ALUMINUM CONCENTRATION, ng/m³

material. Inositol phosphates are present in terrestrial plants and in soils and may be produced not only by plants but by bacteria (Black, 1968). Inositol phosphates have been identified in samples of fresh water (Herbes et al., 1975) but have not yet been detected in the oceans.

Another possible source of acid soluble phosphorus might be the polyphosphates known to be present in bacteria. Polyphosphate chains of up to 300 to 500 units in length are found in bacteria and algae (Zajic, 1969). Bacteria are known to be highly concentrated in the surface microlayer of the ocean (Sieburth, 1965; Sieburth et al., 1976), while the ability of bursting bubbles to inject water droplets containing bacteria into the atmosphere has been well documented (Blanchard and Syzdek, 1970; Bezdek and Carlucci, 1972). However, without additional data it is not possible to state with any certainty that either of the types of phosphorus compounds discussed above are present in the marine atmosphere.

Factor 2 associates the aluminum and reactive phosphorus variations and indicatesa crustal source for this factor. Reactive phosphorus concentration generally increases with increasing aluminum concentration, though there is a large amount of scatter in the data. The data are plotted in Fig. 3. Multi-variate linear regression of the pooled data gives a significant (99.7%) regression of reactive phosphorus on aluminum. The regression coefficient for aluminum is 0.0082 ± 0.0025. This value is reasonably close to the values of 0.009 to 0.015 found for the ratio of phosphorus to aluminum in soils and crustal material (Rahn, 1976).

That crustal material is the main source of reactive phosphorus further supported by comparing the ratios of reactive phosphorus and aluminum in Hawaii to the same quantities in Samoa. These ratios are 1.9 and

2.2 respectively. The trajectories of the air masses which were sampled at the Hawaiian site have been obtained from NOAA. The NOAA Geophysical Monitoring for Climatic Change (GMCC) group provided me with six-hourly near-surface (300 to 1200 m) air parcel trajectory analysis. The trajectories were computed using the Regional-Continental Scale Trajectory Program developed by the Air Resources Laboratory and described by Heffter et al. (1975). These trajectories indicate that the most likely source of crustal material is the North American continent between Canada and Mexico. Some of the acid soluble phosphorus variation also appears to be associated with Factor 2 and may represent phosphate minerals in the crustal material.

Air mass trajectory data are not available for the Samoa site. However, inspection of surface wind and pressure charts suggests that the desert areas of Chile and Peru are possible sources of the crustal material in the Samoa samples.

The persulfate releasable phosphorus stands alone as the third factor. Over all, this phosphorus fraction appears to have little association with either sea salt or crustal material, although there is some aluminum variation associated with the persulfate fraction of the Samoa samples.

The persulfate releasable fraction could include both organic and dilute acid soluble inorganic phosphates. To determine if a significant amount of dilute acid soluble phosphate was present in this fraction, nine Samoa filters were extracted with 0.025 N HCl (pH ≈1.6) and the extracts analyzed for phosphorus. The amount of phosphorus recovered was somewhat less than the recoveries from the persulfate analysis (Table 6). Thus it appears that the phosphorus recovered in the persulfate fraction is entirely organic in nature.

Table 6. Extraction studies of Samoa filter samples

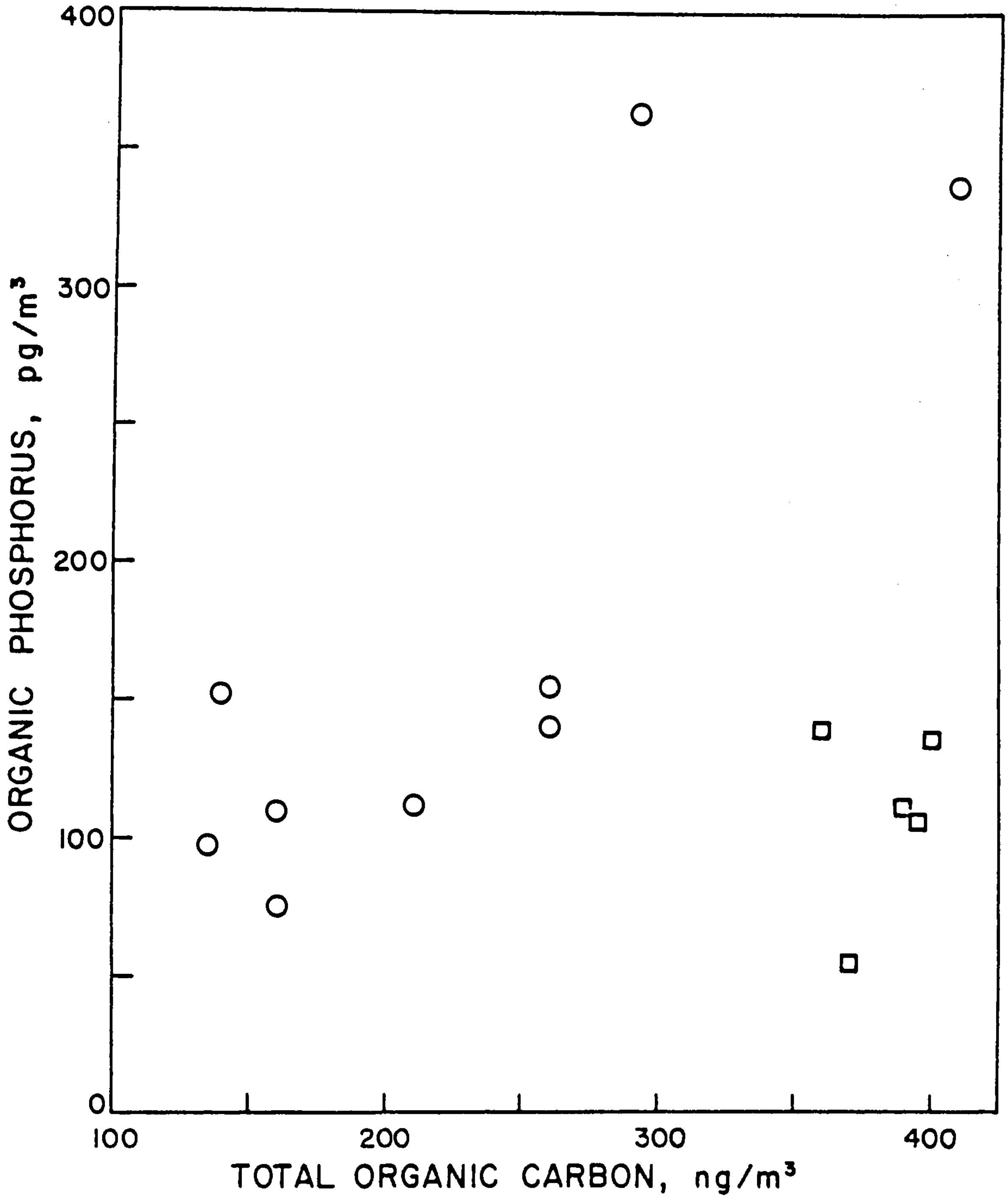
Extraction Method	Phosphorus found pg m^{-3}
0.025 N HCl	40 ± 20
Deionized Water	70 ± 50
Persulfate Oxidation	220 ± 140

Large particle biological material, which would be expected to contain organic phosphorus, has been reported over both the Atlantic and Pacific Oceans (Delany et al., 1967; Folger, 1970; Prospero and Bonatti, 1968). These particles have been identified as marine and freshwater diatoms, fungal spores, phytoliths, and pollen grains. Because of their lower densities and irregular shapes, large organic particles are likely to be transported much farther than mineral grains or salt particles of equivalent size.

It appears however, that approximately 80% of the total organic carbon (TOC) in the marine atmosphere at both Hawaii and Samoa is found on particles less than 0.5 μm in diamter (Hoffman and Duce, 1977). This size fraction, then, is also a possible source of organic phosphorus. Due to the very low levels of total phosphorus on the impactor samples, it was not possible to determine organic phosphorus as a function of particle size directly. However, from the data presented in Table 3 and in Figures 2 and 4, some inferences can be made. The concentration of organic phosphorus in the marine air of Samoa in the rainy season was about one half of the concentration in the dry season. This would suggest that these particles were effectively removed by rainout in the wet season, and so were relatively large since removal by rain is more efficient for larger particles (Gatz, 1975).

Figure 4 shows that if two anomalous Samoa points are excluded, there is little correlation between the organic phosphorus and the organic carbon concentrations of Hoffman and Duce (1977) measured on simultaneous samples. The TOC in the marine air at Samoa was about one half of the concentration found in Hawaii. Organic phosphorus levels, on the other hand, were very similar. The two samples at Samoa with high organic phosphorus and TOC

Fig. 4 The concentration of organic phosphorus vs. total organic carbon in the marine air of Hawaii and Samoa. □- Hawaii, ○- Samoa.


ORGANIC PHOSPHORUS, pg/m³
0
100
200
300
400
TOTAL ORGANIC CARBON, ng/m³
100
200
300
400

values were the first two samples taken at the start of the dry season sampling period, and it is possible that these samples are contaminated with construction debris. The impactor data, however, indicate that some fraction of the organic phosphorus may be associated with the fine fraction of organic carbon. The increase in total phosphorus on the impactor backup filter may be related to the large mass of fine particle organic carbon also found on the impactor filters.

In summary, the data suggest that the organic phosphorus input to these islands is mostly biologically derived particles of greater than 0.5 μm in diameter, but that some small fraction may be associated with the 80% of the organic carbon which is found to be less than 0.5 μm in diameter.

INPUT OF PHOSPHORUS TO THE WINDWARD VEGETATION

The measured input of total available phosphorus is estimated to be 0.14 kg $ha^{-1}yr^{-1}$ based on the precipitation samples taken at Samoa. However Ungemach (1972) points out that it is not easy to distinguish true input from simple recycling of locally derived material, especially in the tropics where biological activity is intense. A calculation of input based on atmospheric concentrations, deposition velocities, and rainout factors should permit me to estimate the amount of recycled material present in the precipitation samples.

The particle size distribution used in my calculation is that obtained for total phosphorus on the Hawaiian impactor sample. Using this distribution, the average wind velocity at the time of sampling, and the data on the deposition velocity as a function of particle size and wind velocity of Sehmel and Sutter (1974), I obtain a weighted average deposition velocity of ≈3 cm/second. This is in reasonable agreement with the average deposition velocity of 2.4 cm/sec for phosphorus compounds measured in an English woodland by White and Turner (1970). It is significantly higher than the value of 0.6 cm/sec by Delumyea and Petel (1977) for deposition of phosphorus compounds over Lake Huron. However, the mass median diameter of particles sampled by Delumyea and Petel was less than 1 μm vs ≈3 μm for my Hawaiian sample. The differences in deposition velocity are consistent with this difference in diameter.

Based on a deposition velocity of 3 cm/sec and an atmospheric concentration of 500 pg m^{-3} a dry deposition flux of ≈5 g $ha^{-1}y^{-1}$ is obtained. Additional input will occur in rainout and washout. I can estimate the wet input using the data of other investigators on the wet/dry input ratio of phosphorus at other locations. Nihlgard (1970) and Kluesener (1972) have measured precipitation and dry fallout inputs in Sweden and Wisconsin, areas which have rainfalls of ≈80 cm/year. Ratios of phosphorus input in precipitation to that of dry fallout are 0.33 and 0.65 respectively. White and Turner (1970) find a ratio of 2.85 for an English woodland with a rainfall of 155 cm. Cape Matutula, Samoa where both the filter and bulk precipitation samples were taken, has an estimated rainfall of 250 cm/year. Based on this rainfall, I estimate the ratio of phosphorus input by precipitation to that of dry fallout to be between 4 and 5. This gives a total phosphorus input of 0.025 to 0.030 Kg $ha^{-1}y^{-1}$. This amount is approximately 20 to 25% of the 0.14 Kg ha^{-1} y^{-1} phosphorus input estimated from the bulk precipitation analysis and suggests that perhaps 75 to 80% of that phosphorus content was from recycling of locally derived material.

Williams (1967) has reported the results of a phosphorus analysis on one rain sample taken on shipboard 30 miles north of Samoa. The phosphorus concentration was found to be 2.5 $\mu g\ l^{-1}$. The composition of the phosphorus was 50% reactive, 50% organic. Based on rainfall of 133 cm/year over the oceans at this latitude (Baumgartner and Reichel, 1975) and an estimated rainout to dry deposition ratio of 3:1, I obtain a phosphorus input of 0.045 Kg $ha^{-1}y^{-1}$. Since this estimate is based on only one sample, it is a tenuous number. However, it appears that a true phosphorus input rate for these islands is certainly less than 0.1 Kg $ha^{-1}y^{-1}$ and most likely less than 0.05 Kg $ha^{-1}y^{-1}$. While this input of phosphorus is small compared to the amounts reported in continental areas, it may be important to the nutrient balance of the island vegetation. The intense rainfall (up to 500 cm/year) on the windward side of these islands results in strongly leached acid soils. Under these conditions, the soil phosphorus below the humus layer is tightly fixed and unavailable. Atmospheric input may be significant in balancing the nutrient losses that occur from runoff or fixation.

SUMMARY

The concentration of phosphorus in the prevailing trade winds of the Hawaiian and Samoan islands ranges from 300 to 800 pg m^{-3}, averaging about 500 pg m^{-3}. Reactive phosphorus comprised 20 to 35% of the total, organic phosphorus 20-35%, and acid soluble phosphorus 40-60%. Factor analysis suggests that the source of the reactive phosphorus is crustal material, while the acid soluble phosphorus fraction may be derived from the surrounding oceans. The source of organic phosphorus is more complex. This fraction is most likely biological particles from either continental or oceanic sources. It appears to have a fairly large particle size and

is not a major portion of the total organic carbon content of the marine air at these sites.

The net phosphorus input to the vegetation on the windward sides of these island chains is estimated to be .025 to 0.030 Kg $ha^{-1}y^{-1}$, based on the atmospheric concentration, a calculated deposition velocity and an assumed ratio of input in precipitation to that in dry fallout. This value amounts to 15 to 20% of the phosphorus deposition measured in a bulk precipitation collected at an island site. I conclude that bulk precipitation samples are easily contaminated in tropical regions where biological activity is intense.

ACKNOWLEDGEMENTS

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THE TRANSPORT OF PHOSPHORUS TO THE NORTH ATLANTIC BY THE SAHARA DUST PLUME

ABSTRACT

The concentrations of phosphorus and iron have been measured in the marine air over the North Atlantic between 15°N and 25°N. Dust from the Sahara desert region of North Africa is transported to the Atlantic Ocean in this 10° latitude band. Iron concentrations of between 2700 and 6600 ng m^{-3} were measured in the atmosphere east of longitude 40°W, indicating a high concentration of dust in this region. Phosphorus concentrations east of 40°W ranged from 44-82 ng m^{-3} compared to 2-8 ng m^{-3} in areas of low iron concentrations. Samples collected in the region of high dust concentration had a P/Fe ratio of 1.2×10^{-2}, in good agreement with the P/Fe ratio on the <16 μm radius fraction of desert soils from Libya. It is estimated that 130 μg of phosphorus are released for every gram of Sahara dust that falls into the mixed layer of the ocean. Using a previously developed model for the transport of Sahara dust to the North Atlantic, the input of nutrient phosphorus to the mixed layer is estimated to range from 1230 μM $m^{-2}y^{-1}$ near the African coast to 10 μM $m^{-2}y^{-1}$ 5000 km from the coast. The atmospheric input of soluble phosphorus near the coast is insignificant compared to the estimated input to the surface waters from upwelling. However the atmospheric input in the nutrient poor waters 1000-2000 km from the coast may be of the same order of magnitude as diffusive input from deep water.

ATMOSPHERIC PATHWAYS OF THE PHOSPHORUS CYCLE

INTRODUCTION

Junge (1956) suggested that the reddish yellow dust observed on samples of atmospheric particulate matter collected in Florida might have been transported across the Atlantic from the Sahara desert. The first major study of this material was made by Delany et al.(1967) at Barbados. Since then the nature of the dust material has been the subject of continuing investigations both at Barbados (Prospero, 1968; Prospero et al., 1970; Carlson and Prospero, 1972; Prospero and Carlson, 1972) and on shipboard in the North Atlantic (Jaenicke et al., 1971; Schütz, 1977; Lepple, 1975). These investigations have concentrated on the determination of mass transport, particle size distribution, and the mineralogy of the insoluble fraction of the dust. Much less attention has been paid to the nutrient fraction of the dust plume. While some studies on the release of phosphorus upon contact of aerosol particles with sea water have been reported by Lepple (1974) and Nehring (1976), no estimates of the total input of any nutrient materials to the Atlantic Ocean by the Sahara plume are available.

Nutrient supply through the atmosphere could be of particular importance for tropical waters. The waters of the Atlantic at 20°N are thermally stratified throughout the year (Ryther, 1963). Under this condition, the most likely supply of nutrients to the euphotic zone is diffusion and advection through the thermocline or fallout from the atmosphere. Thus atmospheric input of nutrients may be significant in sustaining the productivity that occurs in this region. Phosphorus is likely to be the nutrient contributed in greatest quantity by the Sahara plume. Abundant phosphate deposits exist in western North Africa and phosphorus, unlike nitrogen, has no significant gaseous components in its cycle.

In this paper I will make an estimate of the flux of soluble phosphorus by airborne Sahara dust to the North Atlantic and compare this estimate with the phosphorus flux to the mixed layer from the underlying deep waters.

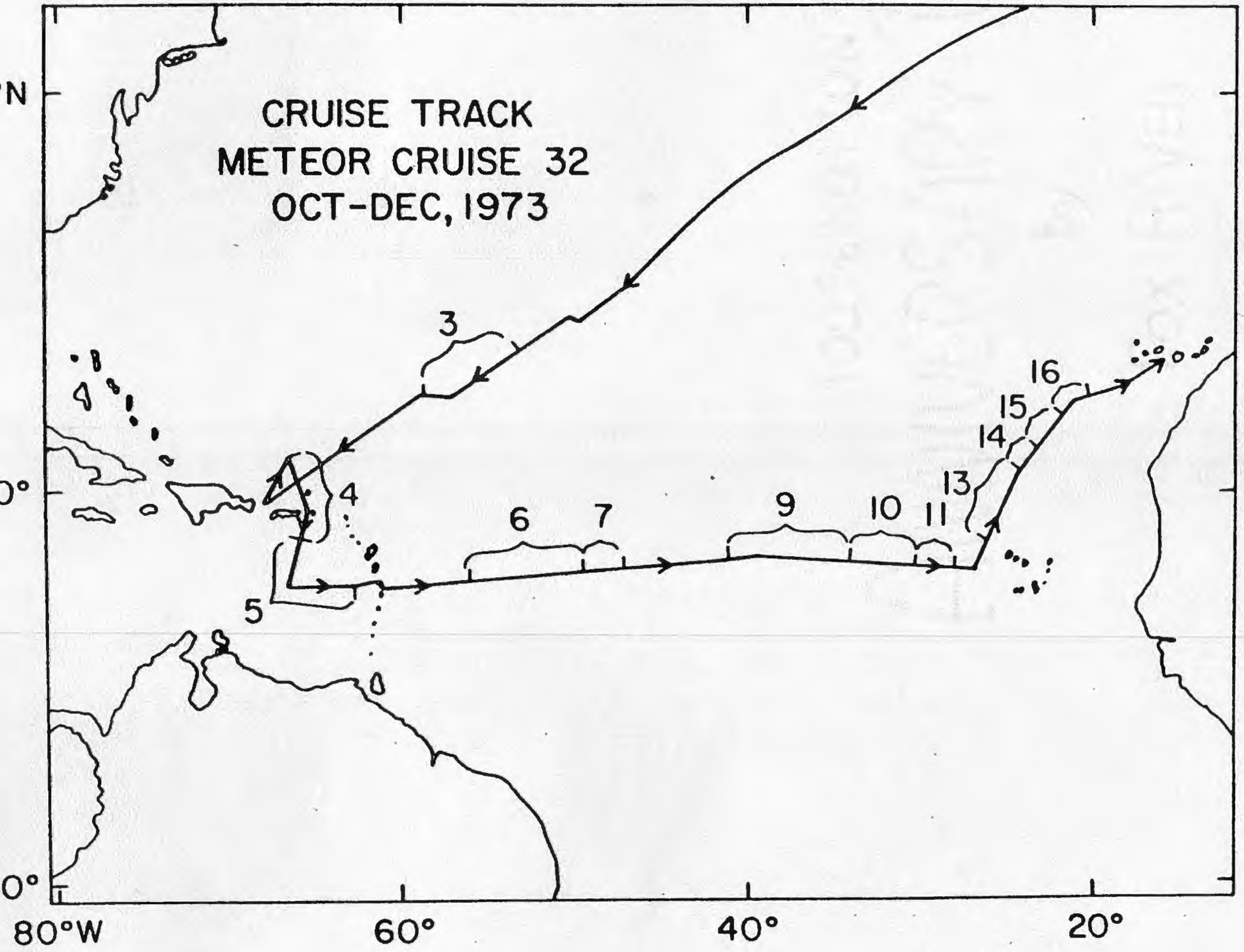
SAMPLING AND ANALYTICAL METHODS

Samples of atmospheric particulate matter over the Atlantic Ocean were obtained by L. Schütz on cruise #32 of the Federal Republic of Germany's R/V METEOR during October, November and December of 1973. The cruise track and sample locations are shown in Figure 1. The samples were collected on Delbag Microsorban 97/99 filters (20 x 25 cm) using GSA 3-S6 Magnetic high-volume pump. Delbag filters are reported to be 99% efficient in the removal of particles $\gtrsim 0.3$ µm in diameter (Dams et al., 1972). The sampling was done under quasi-isokinetical conditions. Sampling volumes ranged between 2700 and 6700 m^3 of air.

In addition to the ocean samples, samples of desert soil and dustfall were collected at Camp Derj and at Sebha Oasis in the Libyan Arab Republic. For details of the collection and particle size analysis of these soil samples see Schütz and Jaenicke (1974).

Discs of 2.5 diameter were punched from the filter material and analyzed for phosphorus and iron. Total phosphorus was determined by ashing of the filter discs at 550°C in the presence of excess magnesium to prevent loss of phosphorus. The residue was dissolved in 1 ml of 1N HCl, diluted to 5 ml with deionized water, and filtered. After dilution to 40 ml with deionized water, phosphorus was determined by the method of Murphy and Riley (1962). Laboratory studies using commercially available iron and calcium phosphates show that these materials were completely recovered by this approach. Only 50% of an aluminum phosphate was recov-

Fig. 1 Cruise track of R/V METEOR cruise and location of the aerosol filter samples.


CRUISE TRACK
METEOR CRUISE 32
OCT-DEC, 1973
40°N
20°
0°
80°W
60°
40°
20°
3
4
5
6
7
9
10
11
13
14
15
16

ered however. The recovery of phosphorus which is occluded or substituted in silicate minerals is not known.

Organic and deionized water soluble phosphorus fractions were determined on four of the filter samples taken directly in the Sahara plume. Organic phosphorus was determined as the difference between the phosphorus content of a sample disk oxidized with potassium persulfate (Menzel and Corwin, 1965) and the content of a similar disk extracted with 0.025 N HCl. Water soluble phosphorus was determined by extraction of the disks with doubly deionized water (pH ≈6).

Soil samples were separated in two fractions, greater than and less than 16 μm radius. Five to 200 mg portions of soil were analyzed for phosphorus by methods similar to those used for the filter samples. In addition, to estimate the release of phosphorus in sea water, samples of soil were agitated in low-phosphorus Sargasso Sea water (pH ≈8.2) for 1 hour, then aged for 12 hours before filtration. Analysis for phosphorus was by the method of Murphy and Riley (1962).

Iron was determined by neutron activation analysis using the Triga reactor at the Johannes Gutenberg University of Mainz. The iron analyses were done by K.A. Rahn. Samples of soil were irradiated for 7 hours at a flux of 7×10^{11} n $cm^{-2}s^{-1}$ and counted one month later using a Ge(Li) detector (50 cm^3 volume, 2.5 KeV resolution) connected to a 4000 channel Intertechnique analyzer. Count times ranged from 4 to 16 hours. 2.5 cm discs of the aerosol filter samples were irradiated for four seven hour periods and counted in the same way as the soil samples. Standards and blanks were prepared and analyzed in the same manner as the samples. Uncertainties are estimated to be ± 15% for the phosphorus analysis and ± 10% for the iron analysis.

RESULTS AND DISCUSSION

The results of the soil and aerosol analyses are presented in Tables 1 and 2 and in Figure 2. The influence of the Sahara plume on the composition of particulate air samples can be seen between filters 7 and 15. Both the iron and phosphorus concentrations increase by one to two orders of magnitude in concentration in these samples as compared to the concentrations found in the samples from outside the plume (3 through 6). The P/Fe ratios in the plume agree well with those calculated for the two desert samples. These ratios are significantly lower than those found for the samples obtained outside the plume. The P/Fe ratios of the non-plume samples agree well with ratios of between 25 and 100 observed in aerosol samples from the western North Atlantic (Graham, this thesis, Chap. 4).

While the ratios of P/Fe in the aerosol samples from the Sahara plume are similar to those in the Libyan desert samples, the aerosol samples contain a much higher proportion of water soluble phosphorus (Table 3). Organic phosphorus was detected in only one aerosol sample (#13). No organic phosphorus could be detected in the other three plume aerosol samples or in the Libyan soil samples. However, Lepple and Brine (1976) report that eolian dust from the Sahara contains about 3% organic carbon by weight. Thus the presence of some organic phosphorus would seem probable.

Release of phosphorus in sea water

About one third of the acid soluble phosphorus in the plume aerosol samples is soluble in doubly distilled water. This compares to a solubility of only 3% for the Libyan soil phosphorus. The finest fraction of the

TABLE 1. Phosphorus and Iron in Libyan Soils

Soil Sample	Location	Origin	Particle Radius - μm	Fe ppm	Water Sol. P P-ppb	Acid Soluble P-ppb	Water Sol. P % of Acid Sol. P	Acid P/Fe $x10^3$
12	Sebha	Wind eroded surface	> 32	5,500	2	60	3.9	10.9
			< 32	46,000	18	570	3.2	12.4
39	Camp Derj	Dust storm fallout	> 32	12,000	3	100	3.0	8.3
			< 32	32,400	23	740	3.1	22.8

TABLE 2. Phosphorus and Iron Content of Aerosol Samples

Sample #	Dates Sampled	Iron ng/m3	Total Phosphorus ng/m3	P/Fe x10^3
3	Oct 25-27	98	4.2	43
4	Nov 8-10	270	7.9	28
5	Nov 10-12	58	3.4	65
6	Nov 18-20	40	2.3	58
7	Nov 20-21	660	18	26
9	Nov 25-27	3910	56	14
10	Nov 27-28	2700	44	16
11	Nov 28-29	4100	82	20
13	Nov 30-Dec 1	3200	49	15
14	Dec 1-2	6600	56	9
15	Dec 2-3	4300	54	12
16	Dec 3-4	390	15	38

Fig. 2 Concentrations of iron and phosphorus and the phosphorus iron ratio for aerosol samples collected over the North Atlantic

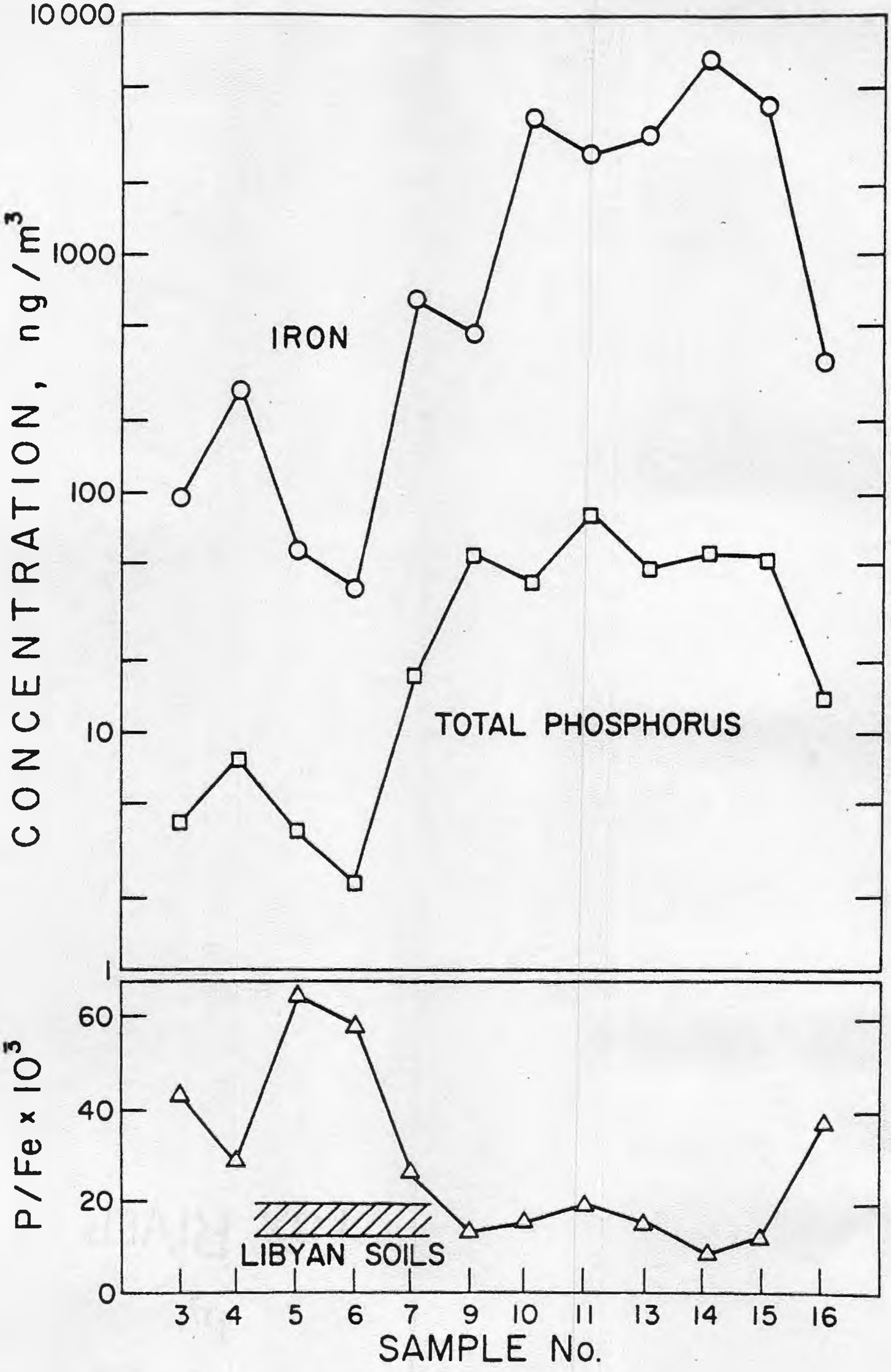

10 000
1000
100
10
1
CONCENTRATION, ng/m³
IRON
TOTAL PHOSPHORUS
60
40
20
0
P/Fe × 10³
LIBYAN SOILS
3
4
5
6
7
9
10
11
13
14
15
16
SAMPLE No.

TABLE 3. Phosphorus fractions of Sahara aerosol

Filter Sample	Organic P-ng/m^3	Water Soluble P-ng/m^3	Total P-ng/m^3	Water Soluble P % of Total P
10	NF	16	44	33
11	NF	30	82	37
13	16	22	49	44
14	NF	17	66	30
MEAN		21	60	36

NF - not found

Libyan soils that could be obtained by dry sieving is still much coarser than the dust collected over the Atlantic. Probably a winnowing effect is operating. Schütz (1977) shows that essentially all particles larger than 10 μm in radius fall out of the plume within the first 1000 km of transit over the ocean. The greatest portion of these are lost in the first 500 km. I would thus expect to find that the finest, most soluble fraction of phosphorus is transported furthest over the ocean.

Most of the phosphorus deposited in the Atlantic from the Sahara is not soluble and therefore not available as a nutrient. Estimating just what fraction of the total phosphorus will become available in sea water is highly subjective, depending on the particle size of the aerosol and its settling rate, the turbulence of the mixed layer, and the existence in the oceans of processes such as bubble flotation of mineral grains. The data presented in Table 4 shows that release of the phosphorus contained in Sahara dust does occur. The release appears to be both time dependent and sensitive to the differences in pH and ionic strength between sea water and distilled water. After 12 hours about twice as much phosphorus is released in deionized water at a pH of 6 as in sea water at a pH of 8-8.3. A study by Nehring (1976) shows that, at much longer times, the release of phosphorus into sea water approaches the amount released in deionized water.

The amount of phosphorus released in sea water by the Libyan soil and dustfall samples agrees well with the release observed by Nehring (1976) for his sample of dustfall (Table 4). The samples collected by Lepple (1975) show a higher release from 130 to 330 μg P per gram of dust. If I assume that:

TABLE 4. Solubility of Phosphorus from Sahara Soil and Dust Samples

Sample - Particle Diameter	Extraction Time	Phosphorus Extracted µg/g dust		Ratio of P extracted Sea Water/Deionized Water	Reference
		Deionized Water	Sea Water		
Sebha Soil - Libya, <32 µm	12 hours	27.6 ± 6.6	18.3 ± 8.0	0.66	This paper
Camp Derj Dust Fall- <32 µm Libya	12 hours	25.4 ± 7.8	10.8 ± 1.4	0.42	This paper
Dustfall between Cape Vert and Cape Blanc	12 hours	28.8	17.4	0.61	Nehring (1976)
"	34 days	48.1	45.0	0.94	Nehring (1976)
"	123 days	49.6	49.3	0.99	Nehring (1976)
Dakar dune soil, 10-20 µm	12 hours	-	130	-	Lepple (1975)
Spanish Sahara soil, 37 µm	12 hours	-	130	-	Lepple (1975)
Filter sample near Dakar	12 hours	-	220	-	Lepple (1975)

1. 36% of acid soluble phosphorus in the Sahara dust samples over the Atlantic is distilled water soluble (Table 3),
2. 55% of the water soluble phosphorus fraction is released on contact with sea water (Table 4),
3. The dust plume contains 700 μg acid soluble P per gram of dust,

I estimate that 130 μg of phosphorus are released to sea water for every gram of dust which falls on the ocean surface.

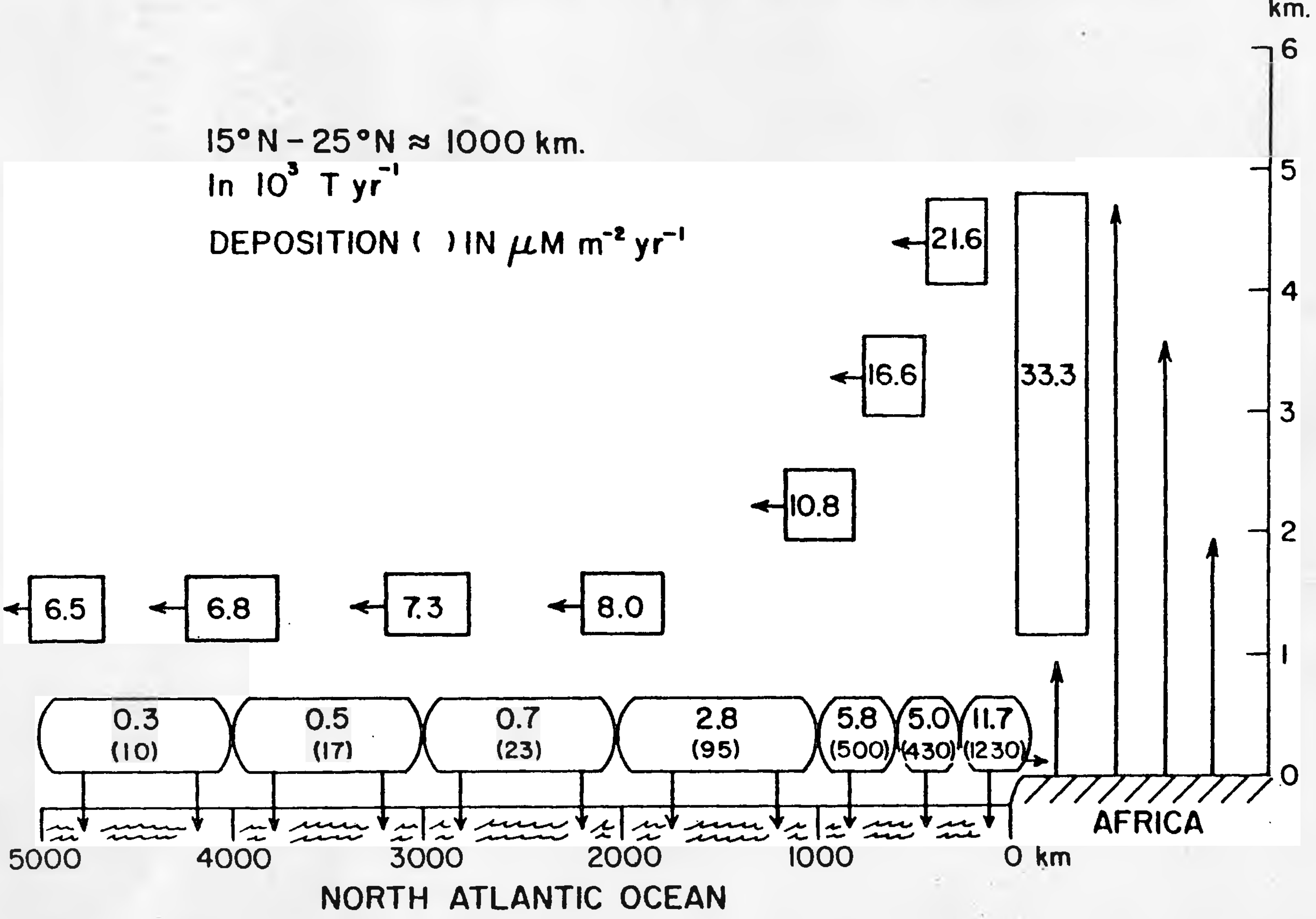
Flux of soluble phosphorus

Schütz (1977) has developed a steady state model for the transport of eolian material from the coast of Africa across the Atlantic between 15°N and 25°N. The model uses steady state transport equations which include horizontal zonal transport of the aerosol particles by wind and vertical transport by sedimentation and turbulent diffusion. The model uses the specific flow conditions of the NE tradewind zone and is able to explain the observed particle size distribution and particle concentration data.

Using this model Schütz and Jenicke (1977) have estimated the annual transport of dust down this 10° latitude band to be about 260 x 10^6 T yr^{-1} at the coast of Africa. At a point 1000 km from the coast, the transport is estimated to be 83 x 10^6T y^{-1}, while approximately 50 x 10^6 T yr^{-1} is estimated to travel past Barbados at longitude 60°W which is 5000 km from its departure point at the African coast. I have used this model to estimate the flux of nutrient phosphorus in the dust plume, by assuming that 130 μg of soluble P are carried by each gram of Sahara dust to the surface of the ocean. The resulting transport and fallout fluxes are shown in Figure 3. Input ranges from about 1200 μM $m^{-2}yr^{-2}$

Fig. 3 Transport of soluble phosphorus to and over the North Atlantic from Africa. Numbers in ( ) are the deposition rates of soluble phosphorus in $\mu M\ m^{-2}y^{-1}$.

SOLUBLE PHOSPHORUS TRANSPORT AND DEPOSITION



near the African coast to 13-110 μM m^2 yr^{-1} in the Sargasso Sea area between 1000 and 5000 km from the coast (roughly 27°W to 67°W).

I can also estimate the input of phosphorus to the North Atlantic more directly in a portion of the region under the dust plume. Aerosol samples 10, 11, 13 and 14, collected between 25°W and 35°W, contain 21 ng/m^{-3} of water soluble phosphorus on the average. Assuming a deposition velocity of 1 cm sec^{-1} as a first approximation, I calculate the fallout of distilled water soluble phosphorus to be 2.1×10^{-14} g cm^{-2} sec^{-1} or the equivalent of 200 μM $m^{-2}y^{-1}$. If 50% of this phosphorus is released in sea water, the input of dissolved phosphorus into the mixed layer of the ocean is 100 μM P $m^{-2}y^{-1}$, in reasonable agreement with the input calculated for 1000-2000 km from the African coast using the transport model.

The input of insoluble phosphorus compounds is probably an order of magnitude greater than the flux of soluble phosphorus. Glaccum (1977), using emission spectroscopy, finds between 1600 and 2200 μg P gm^{-1} of Sahara aerosol. Lepple (personal communication) has found an average of 2000 μg gm^{-1} in Sahara aerosol samples analyzed following digestion with hydrofluoric acids. These results are two to three times higher than the values I find for the <32 μm diameter Libyan soils and may reflect the input of high apatite dust from the northwest coast of Africa, the fact that each study used a different analytical method, or both factors.

Inputs to the Mixed Layer

The input of soluble phosphorus near the West African coast appears to be negligible compared to the input from the upwelling that occurs in the coastal waters. Using an average upwelling velocity of 10^{-2} to

10^{-3}cm sec^{-1} (Mittelstaedt et al., 1975) and a phosphorus content of the surface water of 0.3 μM 1^{-1} (Szekielda and Ballestes, 1974), the phosphorus input by advection alone is on the order of 100-150 mM $m^{-2}yr^{-1}$.

The input of phosphorus through the permanent thermocline of the Sargasso Sea can only be estimated very crudely. The magnitude of the eddy diffusion coefficient to be applied is subject to great uncertainty. Microstructure investigations in the central gyres of the Pacific give values of the eddy diffusion coefficient k of 0.6 to 2.3 x 10^{-6} m^2 sec^{-1} (Gregg et al., 1973; Gargett, 1976) in the thermocline. However Schmidt and Evans (1977) suggest that salt fingering can result in significant mixing in the permanent thermoclines of the central gyres. The mixing due to salt finger formation is equivalent to an eddy diffusion value k of about 1 x 10^{-5} m^2 sec^{-1} for salt (but not for heat). Thus it appears that salt fingering may increase diffusive transport across the thermocline by an order of magnitude.

The actual sign and velocity of advection that occurs through the thermocline is also subject to much uncertainty. Stommel and Webster (1962) have suggested that Ekman transport may cause subsidence of the surface waters. Under these conditions no advection into the surface layer would occur. For purposes of comparison with the input of soluble phosphorus from the atmosphere, I assume no advection. Phosphorus concentration for the surface and deep waters in the area between 15-25°N and 26-60°W are taken from stations occupied during the DISCOVERY II and CRAWFORD IGY cruises (Worthington, 1958; Metcalf, 1958). Fluxes of phosphorus through the thermocline using these data are between 70-170 μM m^2yr^{-1} when an eddy diffusion coefficient k of 10^{-6} is used. This is about the same order of magnitude as the atmospheric flux. Using k equal to 10^{-5} yields an input ten times larger, with the atmospheric input droping to 10% or less of the input through the thermocline.

Besides phosphorus, Sahara dust can also carry nitrogen compounds which are soluble in sea water (Nehring, 1976). The N/P ratio in the sample analyzed by Nehring is 16/1. Thus it appears that both essential nutrients for plankton growth are present in Sahara dust. The input of Sahara dust into the ocean appears to follow an annual cycle with a summer maximum and a winter minimum (Prospero, 1968; Carlson and Prospero, 1972; Prospero and Nees, 1977). A study of the nutrient content and productivity of waters under the Sahara plume might show fluctuations which can be associated with dust fall intensity.

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THE ATMOSPHERIC TRANSPORT OF PHOSPHORUS TO THE WESTERN NORTH ATLANTIC

ABSTRACT

The concentration of particulate phosphorus in the atmosphere has been measured over the western North Atlantic and at the island of Bermuda. Phosphorus concentrations ranged from 57 ng m^{-3} near the North American coast to 0.6 ng m^{-3} at Bermuda. The average concentration over the western North Atlantic was 7 ng m^{-3}. The phosphorus over this portion of the ocean is evidently contained in particles of crustal material from the North American continent and also possibly from the Sahara desert, in soot and fly ash particles from the burning of fossil fuels in North America, and in sea-salt particles ejected from the surface of the ocean by bursting bubbles. The net input of phosphorus into an area bounded by the North American coast, a line along 25°N latitude, and a line along 65°W longitude is estimated to be between 0.5 and 1.0 x 10^{10} g y^{-1}. About 36% of this phosphorus is estimated to be released upon contact with sea water for a 12 hour period. Thus 2 to 4 x 10^{9} g y^{-1} of nutrient phosphorus are added to the North Atlantic surface waters by atmospheric deposition. This is about 10% of the estimated reverine input of dissolved phosphorus to the same region of the Atlantic Ocean.

INTRODUCTION

Phosphorus is an essential nutrient for the growth of all living things. Consequently the world consumption of phosphate fertilizers has doubled every 10 years (Lerman et al., 1975). The fraction of fertilizer phosphorus that is transported to the oceans annually is unknown. However Stumm (1973) has shown that the concentrations of phosphorus in major European rivers and the quantity of phosphate rock mined annually have both increased exponentially at about the same rate. Both Broecker (1971) and Stumm (1973) have suggested that steadily increasing inputs of phosphorus to the oceans could have undesirable results in coastal areas, including changes in plant and animal life and an increase in the fraction of anerobic waters.

In addition to the transport of phosphorus to the oceans by rivers, phosphorus can also be carried to the oceans through the atmosphere. Until now, however, sufficient data to permit the estimation of the size of this flux have not been available.

In this paper I will present data I have obtained on the concentration of phosphorus in the marine atmosphere of the western North Atlantic and show that the source of this material is mainly crustal and anthropogenic material from the North American continent. In addition I will estimate the rate of input of phosphorus to this portion of the Atlantic Ocean.

METHODS

Samples of atmospheric particulate matter were collected over the North Atlantic on R/V TRIDENT cruises 161 and 168 in December, 1974, and

June, 1975. Additional samples were collected at an atmospheric sampling site on the island of Bermuda from May through July 1975. The samples were collected on 20 x 25 cm Delbag Microsorban 97/99 filters using Cadillac high volume sampling pumps. The filters are reported to have an efficiency of 99% for the collection of particles >0.3 μm in diameter (Dams et al., 1972). The TRIDENT samples were collected using an atmospheric sampling tower mounted on the bow of the ship. Filter holders mounted on this tower were 15 m above the ocean surface and forward of the bow, well in front of any bow spray. To prevent contamination by ship stack emissions, a directional air sampling system was used. Sampling only occurred when the wind was between ± 60° off the bow.

The Bermuda sampling site consists of a 20 m high sampling tower located on the southwest coast of the island. The sampling unit was located at the top of this tower. Sampling only took place during periods of onshore winds. At times of off-shore winds or of precipitation the system was shut down automatically.

After collection of the sample, the filter was quartered and the quarters stored in sealed polyethylene bags and frozen until analysis. Sodium, aluminum, and vanadium were determined by neutron activation. One quarter of the filter was pelleted and irradiated for 30s in the Rhode Island Nuclear Science Center swimming pool reactor at a flux of $4 \times 10^{12} n\ cm^{-2} s^{-1}$. Within two minutes the samples were counted for 400 s on a 20 cm^3 Ge(Li) detector (resolution of 2.3 KeV for the 1332 KeV gamma ray of ^{60}Co, efficiency 7%) coupled to a Nuclear Data 2200 4096 channel analyzer with computer compatible magnetic tape output

(Ampex TM-7). A computer program (J.L. Fasching, personal communication), was used to process the Ge(Li) spectra acquired. Absolute standards for each element were prepared on blank filters, pelleted, irradiated, and counted in the same manner as the unknowns. Constant geometry was maintained during the counting of all standards and unknowns. Corrections were made for dead time and half life discrimination.

Total phosphorus was determined by ashing one quarter of the filter at 550°C in the presence of excess magnesium. The residue was dissolved in 1 ml of 1 N HCl, diluted to 5 ml with doubly distilled (DD) water, and filtered through a 0.2 μm Nuclepore filter to remove insoluble particles. The ashing beaker and filter were rinsed with two 5 ml aliquots of DD water, this was added to the original filtrate. After dilution of the filtrate to 40 ml, any arsenate present was reduced to arsenite by the method of Johnson and Pilson (1972). Phosphorus was then determined by the method of Murphy and Riley (1962). Corrections for filter blanks were made on all samples. Blanks were typically 10% of the sample values.

Reactive phosphorus was determined by extraction of one-quarter of a filter for 30 minutes in 40 ml of DD water. The sample was then filtered through a 0.4 um Nuclepore filter, arsenate reduced, and analyzed for phosphorus.

The difference between the total phosphorus as determined by the ashing process and the water soluble reactive phosphorus is the amount of organic and acid soluble inorganic phosphorus present in the sample. This fraction shall be referred to as AS+O phosphorus.

Analytical precisions were found to vary with the amount of material collected on the filter; precisions were poorer when dust concentrations in the atmosphere were very low. Typical analytical precisions were: total phosphorus, ± 10%, reactive phosphorus, ± 15%, sodium ± 5%, aluminum ± 6%, vanadium, ± 11%.

In addition to the samples collected on Delbag filters specifically for this study, samples collected on Whatman 41 filters during TRIDENT cruises 134, 137, and 145, and on Delbag filters for TR 152 were analyzed for total phosphorus only. The Whatman filters have an efficiency of >90% for the collection of particles >0.5 µm in diameter (Stafford and Ettinger, 1972). Only one quarter of a filter was available for analysis. The procedure was identical to that described above for the analysis of the earlier Delbag filter samples.

Rain and total fallout samples were also collected in the North Atlantic. Two rain samples were obtained on Cruise 168, both at about 32°N, 74°W. Samples of total fallout, i.e., rain and dry fallout, were collected at Bermuda during August, September, and October of 1974 and again in May, June, and July of 1975. The 1975 samples proved to be badly contaminated with insects and were not analyzed.

Both rain and total fallout samples were frozen until the time of analysis. Total phosphorus was determined on these samples using the persulfate oxidation method of Menzel and Corwin (1965) followed by colorimetric analyzing by the method of Murphy and Riley (1962).

RESULTS

Concentrations

The concentrations of total, reactive, and AS+O phosphorus, along with sodium, aluminum, and vanadium from cruises TR 161, TR 165 and Bermuda are given in Tables 1, 2, and 3. The distribution of total phosphorus is illustrated in Fig. 1. The sodium and vanadium values have

TABLE 1. Atmospheric concentrations of phosphorus, sodium, aluminum and vanadium collected on TR 161

SAMPLE NUMBER	DATE COLLECTED	MIDPOINT LOCATION LAT/LONG.	PHOSPHORUS ng m^{-3}			SEA SALT Na^1 μg m^{-3}	Al ng m^{-3}	EXCESS V^1 ng m^{-3}
			TOTAL	REACTIVE	AS+O			
1	12/6/74	32°N/68°W	5.5	2.1	3.4	5.5	10	0.1
2	12/7/74	32°N/70°W	4.3	1.1	3.2	3.8	15	0.1
3	12/8/74	33°N/73°W	4.1	2.3	1.8	5.5	85	1.6
4	12/11/74	33°N/73°W	1.3	0.7	0.6	1.5	63	3.1
5	12/13/74	33°N/74°W	5.0	4.4	0.6	3.7	130	6.8
6	12/15/74	32°N/74°W	9.3	3.0	6.3	4.4	61	3.0
7	12/15/74	31°N/77°W	6.3	2.6	3.7	5.7	51	3.4
8	12/17/74	31°N/78°W	5.1	3.1	2.0	3.9	72	3.1
9	12/17/74	28°N/80°W	9.7	3.7	6.0	7.4	120	3.5
10	12/18/74	27°N/80°W	21.0	5.6	15.4	3.8	270	3.3

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[1] Corrected for crustal Na and V using the ratios of Mason (1966)

TABLE 2. Atmospheric concentrations of phosphorus, sodium, aluminum and vanadium collected on TR 168

SAMPLE NUMBER	DATE COLLECTED	MIDPOINT LOCATION LAT/LONG	PHOSPHORUS ng m^{-3} TOTAL	REACTIVE	AS+O	SEA SALT Na[1] µg m^{-3}	Al ng m^{-3}	EXCESS V[1] ng m^{-3}
1	5/24/75	27°N/78°W	5.4	4.4	1.0	8.7	270	3.4
2	5/25/75	29°N/77°W	5.6	4.4	1.2	0.6	290	2.6
3	5/28/75	30°N/76°W	1.8	0.5	1.3	1.5	99	1.9
4	5/28/75	30°N/76°W	1.8	1.0	0.8	1.7	32	2.5
5	5/29/75	30°N/76°W	1.5	0.6	0.9	1.2	87	1.6
6	5/31/75	32°N/74°W	2.6	0.2	2.4	1.7	31	2.5
7	6/1/75	33°N/73°W	4.3	0.3	4.0	1.9	510	1.3
8	6/1/75	33°N/73°W	4.3	0.6	3.7	2.2	560	1.4
9	6/3/75	35°N/70°W	2.2	1.6	0.6	3.2	110	1.0
10	6/4/75	37°N/70°W	21.7	9.6	12.1	9.2	170	5.4
11	6/5/75	37°N/69°W	17.3	7.5	9.8	10.2	120	3.4
12	6/6/75	36°N/69°W	7.0	5.0	2.0	6.0	220	2.3
13	6/7/75	37°N/68°W	21.9	6.9	15.0	3.6	550	4.1
14	6/8/75	37°N/68°W	4.1	1.6	2.5	8.2	380	0.3
15	6/9/75	39°N/69°W	18.0	6.5	11.5	2.6	140	15.6

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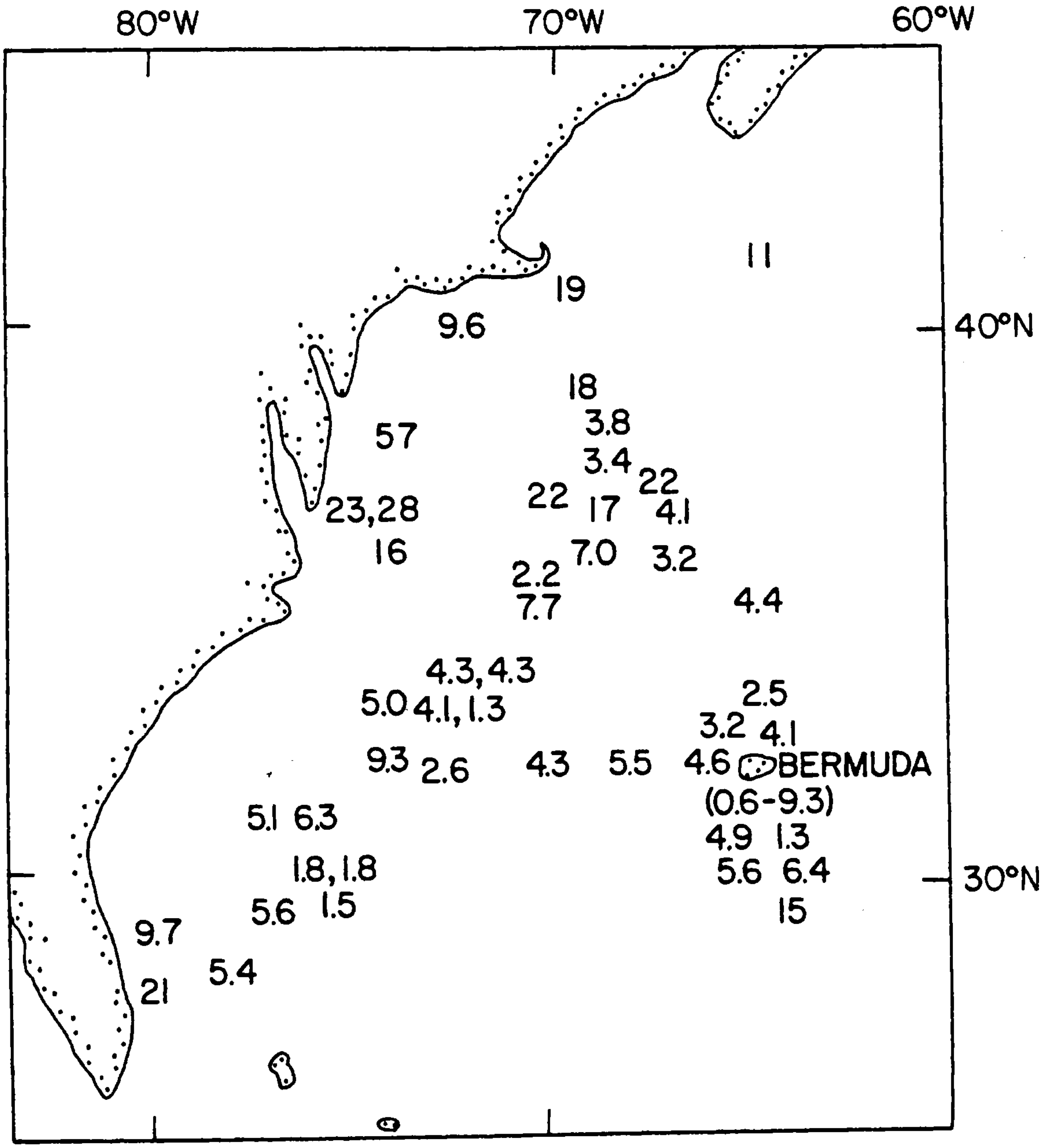
[1] Corrected for crustal Na and V using the values of Mason(1966)

TABLE 3. Atmospheric concentrations of phosphorus, sodium, aluminum and vanadium collected at Bermuda

SAMPLE NUMBER	DATE COLLECTED	AVERAGE[1] TRAJECTORY NO.	PHOSPHORUS ng m^{-3}			SEA SALT Na[1]	Al	EXCESS V[1]
			TOTAL	REACTIVE	AS+O	μg m^{-3}	ng m^{-3}	ng m^{-3}
1	5/21/75	1.8	0.6	0.2	0.4	1.8	12	0.4
2	5/24/75	2.8	0.8	0.6	0.2	2.3	41	0.8
3	5/31/75	3.3	6.1	4.0	2.1	3.2	160	2.3
4	6/7/75	3.2	4.4	1.8	2.6	3.5	120	0.9
5	6/17/75	3.5	7.6	5.9	1.7	2.6	120	2.6
6	6/22/75	3.1	6.4	4.5	1.9	2.7	230	2.7
7	6/29/75	3.4	2.8	1.4	1.4	3.3	230	1.4
8	7/5/75	3.0	9.3	3.0	6.3	2.8	1500	1.3
9	7/9/75	1.5	1.1	0.4	0.7	2.4	120	0.5

[1] Corrected for crustal Na and V using the values of Mason (1966).

Fig. 1 Concentrations of total phosphorus in the marine air of the western North Atlantic in ng m^{-3}.Concentrations in ( ) measured at Bermuda.


80°W
70°W
60°W
40°N
30°N
11
19
9.6
18
3.8
57
3.4
22
22
23,28
17
4.1
16
7.0
3.2
2.2
7.7
4.4
4.3,4.3
5.0
4.1, 1.3
2.5
3.2
4.1
9.3
2.6
4.3
5.5
4.6
BERMUDA
(0.6-9.3)
5.1
6.3
4.9
1.3
1.8, 1.8
5.6
6.4
5.6
1.5
15
9.7
5.4
21

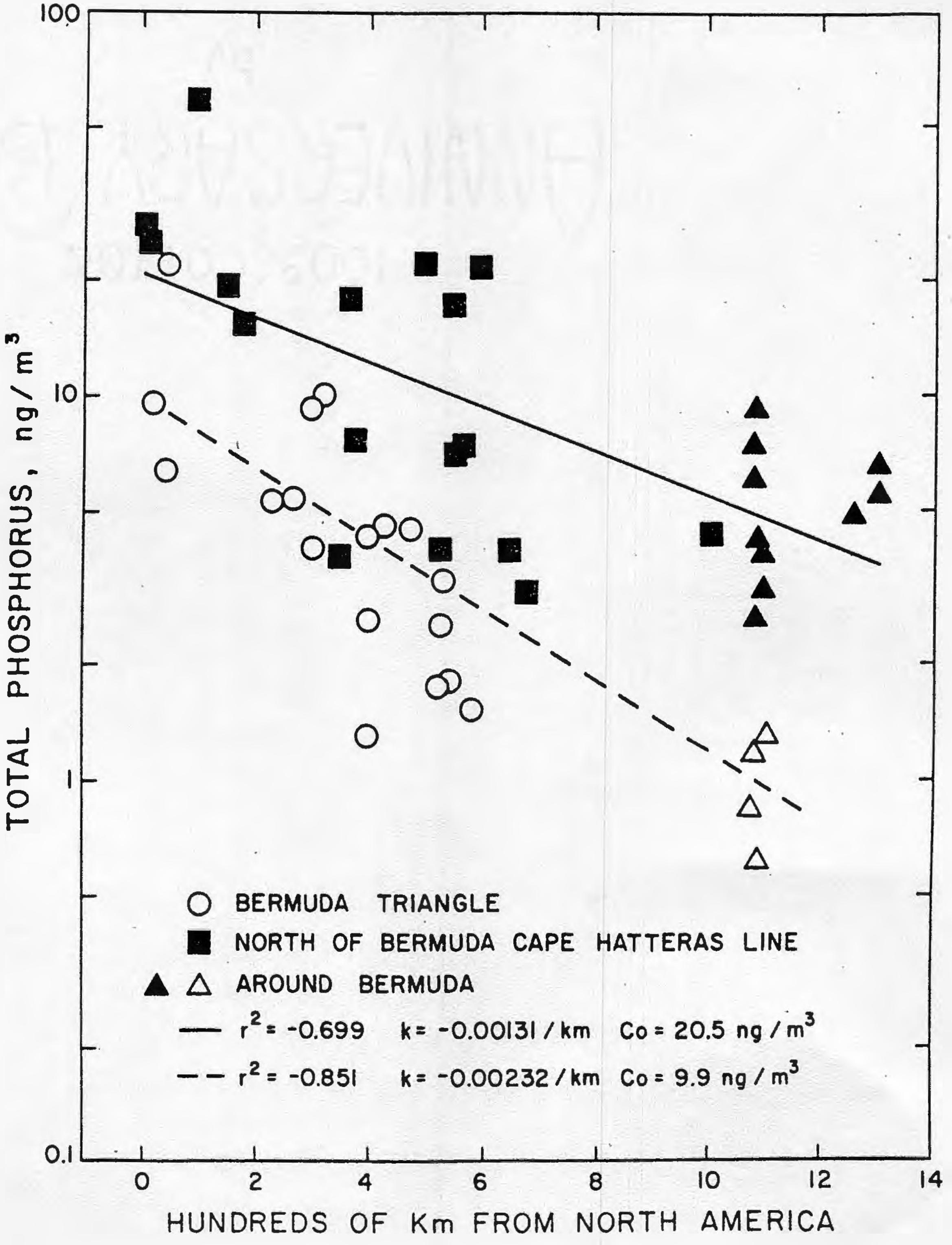
been corrected for a crustal component using the ratios of Na/Al and V/Al in crustal material of Mason (1966). Thus the corrected sodium and vanadium concentrations can be considered to be representative of the amount of sea salt and anthropogenic material present in the samples. Vanadium is an excellent tracer for the emissions from fossil fuel combustion sources (Duce and Hoffman, 1976). These corrected concentrations are referred to as sea salt sodium and excess vanadium respectively. Table 4 lists the concentrations of total phosphorus determined on the samples from cruises TR 134, TR 137, TR 145, and TR 152. These data are also shown in Fig. 1. In general, total phosphorus concentrations appear to be somewhat higher in the region north of a line from Cape Hatteras to Bermuda. This difference between these northern and southern sectors is more clearly illustrated in Fig. 2, where total phosphorus concentration is plotted against the approximate distance of the sample from the North American coast. The analytical results have been separated into two groups; those from samples north of a line between Bermuda and Cape Hatteras (solid squares) and those from samples south of this Cape Hatteras - Bermuda line (open circles). In addition, samples from Bermuda and further east (triangular symbols) also appear to fall into two groups which fit well with the northern and southern sample sets.

The equation $C = C_o e^{-kD}$ has been fitted to each of the sample sets illustrated in Fig. 2. In this equation C is the concentration of phosphorus at any distance D from the coast, C_o is the concentration of phosphorus at the coast, while k is the constant. The regression line through the samples collected north of Cape Hatteras yields a value for C_o of 20.5 ± 4.7 ng m^{-3} and for k of -0.0013 ± 0.0003 Km^{-1}. For the

TABLE 4. Atmospheric concentrations of total phosphorus from samples collected on cruises TR 134, TR 137, TR 145, and TR 152

CRUISE NO.	SAMPLE NUMBER	DATE COLLECTED	MIDPOINT LOCATION LAT/LONG	TOTAL PHOSPHORUS ng m^{-3}
134	1	4/09/73	31°N/66°W	4.9
	2	4/10/73	30°N/66°W	5.6
	3	4/11/73	29°N/64°W	15
	4	4/12/73	30°N/64°W	6.4
	5	4/14/73	32°N/65°W	4.1
	6	4/15/73	30°N/65°W	1.3
137	1	6/05/73	32°N/66°W	4.6
	2	6/06/73	36°N/67°W	3.2
	3	6/07/73	38°N/68°W	3.4
	4	6/08/73	39°N/69°W	3.8
	5	6/09/73	41°N/70°W	19
145	1	10/20/73	32°N/65°W	3.2
	2	10/21/73	34°N/70°W	7.7
	3	10/24/73	36°N/74°W	16
	4	10/25/73	37°N/76°W	23
	5	10/26/73	37°N/76°W	28
	6	10/28/73	38°N/74°W	57
	7	10/30/73	41°N/73°W	9.6
152	1	5/09/74	41°N/65°W	11
	2	5/11/74	35°N/65°W	4.4
	3	5/14/74	33°N/65°W	2.5

Fig. 2 Phosphorus concentration as a function of distance from the North American coast.


100
10
1
0.1
TOTAL PHOSPHORUS, ng/m^3
0
2
4
6
8
10
12
14
HUNDREDS OF Km FROM NORTH AMERICA
○ BERMUDA TRIANGLE
■ NORTH OF BERMUDA CAPE HATTERAS LINE
▲ △ AROUND BERMUDA
— r^2 = -0.699 k = -0.00131/km Co = 20.5 ng/m^3
– – r^2 = -0.851 k = -0.00232/km Co = 9.9 ng/m^3

samples collected below Cape Hatteras, the values are: C_o, 9.9 ± 2.2 ng m^{-3}; k, -0.0023 ± 0.0003 Km^{-1}. The amount of variation (r^2) explained by the regression is 0.70 for the samples north of the Hatteras-Bermuda line and 0.85 for the samples south of this line. The data suggest that the average atmospheric phosphorus content along the northeastern coast is about twice the concentration along the south eastern coast. It also appears that the concentration of phosphorus over the ocean south of Cape Hatteras declines more rapidly with distance than the concentration of phosphorus in the sector north of the Cape Hatteras - Bermuda line.

Deposition rate

The analyses of the total fallout samples collected on Bermuda during 1974 are shown in Table 5. Extrapolating the input of phosphorus during this period to an annual basis gives an estimated input of 0.06 Kg ha y^{-1} . This seems to be a very reasonable value when compared to the measured deposition rates of total phosphorus in eastern North America. Deposition rates over the continent range from 0.2 to 0.9 Kg ha y^{-1} (this thesis, chapter 6).

Rain samples were also collected during two rain squalls which occurred at about 32°N, 74°W during TRIDENT Cruise 161. The samples contained 2 ug l^{-1} and 11.6 ug^{-1} of phosphorus. Blanchard (1963) has estimated that the ratio of aerosol deposition by precipitation to deposition by dry fallout is about 2/1 on a global basis. In this calculation, Blanchard (1963) used 89 cm y^{-1} as the depth of precipitation on a global basis. Precipitation in the Atlantic between 30 and 40°N amounts to less than this, averaging about 63 cm y^{-1} (Baumgartner and

TABLE 5. Deposition rates of phosphorus at Bermuda

SAMPLE	HOURS EXPOSED	PPTU cm	IN PRECIPITATION $\mu g\ l^{-1}$	TOTAL PHOSPHORUS AS BULK DEPOSITION mg ha^{-1} day^{-1}
1	24	0.05	3.4	17
2	24	1.57	1.5	240
3	94.5	0.41	2.7	28
4	18	0.15	3.4	38
5	71	0.79	1.2	33
6	24	1.22	1.1	130
7	96	0.53	4.1	55
8	24	0.74	3.5	250
9	22	1.60	3.3	570
10	25	1.37	2.3	300
11	23	0.94	2.1	200
12	25	4.93	2.5	1200
13	70	1.57	1.8	100
14	24	0.79	1.5	120

Total hours exposed = 564.5

Total input of phosphorus = 3.8 g

Estimated annual input = 0.06 Kg $ha^{-1}y^{-1}$

Reichel, 1975). I will assume a 1:1 precipitation to dry fallout ratio in this region. The annual deposition rates of phosphorus estimated from these two rain samples become 0.03 and 0.15 Kg ha y^{-1} respectively. While these are only very rough numbers, they appear to be in reasonable agreement with the Bermuda estimate.

DETERMINATION OF PHOSPHORUS SOURCES

From factor and regression analyses

I have applied the techniques of factor analysis and multivariate linear regression to the data obtained from the North Atlantic samples. Factor analysis is a statistical technique for the grouping of linear combinations of similar variances from variables that are highly correlated. The theory of factor analysis has been presented in detail by Harman (1967). The results of factor analysis on the concentration of reactive phosphorus, AS+O phosphorus, aluminum, sea salt sodium, and excess vanadium are given in Table 6. Three factors account for 88% of the total variation. The factor containing excess vanadium, which can be considered as an anthropogenic source factor, accounts for the greater part of the variation of both the reactive and the acid soluble plus organic phosphorus fractions. The second factor appears to represent a crustal source as it contains most of the aluminum variation. The third factor contains most of the sea salt sodium variation plus some of the reactive and AS+O phosphorus variations. This factor must represent a marine source.

The results of the factor analysis study suggest that the bulk of the phosphorus variation in the marine atmosphere over the western North Atlantic can be attributed to crustal, marine, and anthropogenic

TABLE 6. FACTOR ANALYSIS OF NORTH ATLANTIC SAMPLES OF ATMOSPHERIC PARTICULATES

	FACTOR 1 ANTHROPOGENIC SOURCE	FACTOR 2 CRUSTAL SOURCE	FACTOR 3 MARINE SOURCE	FINAL COMMUNALITY
Eigenvalues	2.39	1.08	0.91	
Portion	0.48	0.22	0.18	
Cum. Portion	0.48	0.70	0.88	
Variance				
Reactive P	0.77	0.09	0.49	0.84
AS + O P	0.72	0.35	0.33	0.76
Sea salt sodium	0.12	-0.05	0.96	0.94
Aluminum	0.01	0.97	-0.05	0.95
Excess vanadium	0.92	-0.15	-0.10	0.88

sources. These sources can be examined in more detail using multivariate regression analysis (Table 7). This to some extent is an oversimplified approach as it assumes a linear relationship between the variables. The inability to explain more than 40-60% of the total variation suggests that the relationships are more complex. However the regression coefficients do provide me with an estimate of the overall change in phosphorus that should occur with a unit change in sea salt sodium, aluminum, or excess vanadium concentration. These ratios of P/Na, P/Al, and P/V can be compared with data from other sources and appropriate conclusions drawn.

The regression coefficient of total phosphorus with sodium has a value of $(8.4 \pm 2.8) \times 10^{-4}$. This can be interpreted as the ratio of phosphorus to sodium on a sea salt particle ejected from the ocean by the bursting of bubbles. It is in reasonable agreement with the ratios of 1×10^{-4} to 8×10^{-4} found in a field study on Narragansett Bay, Rhode Island. In this study, bay water was bubbled and the resulting ejected droplets of sea water were collected on filters and analyzed for phosphorus and sodium (this thesis, Chapt. 4).

The ratio of total phosphorus to aluminum derived from the regression coefficient can be related to the average quantity of phosphorus associated with a unit of crustal aluminum. The phosphorus may be either organic or inorganic in nature. When the ratio of 0.006 ± 0.002 is compared with the ratio found for samples taken at Narragansett, Rhode Island over a one year period in 1975 (this thesis, Chapt. 6) and with the average of various estimates of P/Al in soil and crust (Rahn, 1976) it is seen to be low (Table 8). It is not apparent whether this low value reflects a crustal source which is low in phosphorus or is the result of phosphorus loss after leaving the coast.

TABLE 7. MULTIVARIATE REGRESSION ANALYSIS OF NORTH ATLANTIC ATMOSPHERIC PARTICULATE SAMPLES

PHOSPHORUS FRACTION	REFERENCE ELEMENT	REGRESSION COEFFICIENT	VARIATION OF COEFFICIENT	SIGNIFICANCE[1] Ho ≠ 0	% VARIATION[2] EXPLAINED	TOTAL VARIATION[3] EXPLAINED
Reactive	Sea salt Na	0.00039	±0.00011	.999	38	57%
	Al	0.002	±0.001	0.85	4	
	Excess V	0.531	±0.101	0.999	58	
Acid Soluble plus organic	Sea salt Na	0.00050	0.00023	0.96	28	
	Al	0.004	±0.002	0.95	18	39%
	Excess V	0.702	±0.213	0.99	54	
Total	Sea salt Na	0.00084	±0.00028	0.99	30	
	Al	0.006	±0.002	0.97	12	54%
	Excess V	1.25	±0.26	0.999	52	

[1] Probability that the coefficient is not equal to zero.

[2] The percentage of the total variation explained by the regression which is explained by a specific tracer.

[3] The percentage of the total sample variation explained by the regression.

TABLE 8. COMPARISON OF TOTAL P/Al RATIOS

LOCATION	ATMOSPHERIC TOTAL P/Al	REFERENCE
Western North Atlantic	0.006 ± 0.002	This paper
Narragansett, Rhode Island	0.011 ± 0.003	Graham (Chap. 6, this thesis)
Average of various crustal and soil values	0.012 ± 0.002	Rahn (1976)

The most unexpected result was the large amount of phosphorus found to be associated with excess vanadium. Many data have been published on the concentrations of vanadium in fuel oil and coal emissions. The difficulty is in locating values for phosphorus in these particles. Smith (1962) has measured both phosphorus and vanadium in fuel oil soot particles; from his data a P/V ratio of 0.2 is calculated. Linton et al. (1976) have measured the phosphorus and vanadium contents, along with other elements, of coal fly ash particles. Bulk concentrations were found to be 600 μg/g for phosphorus and 380 μg/g for vanadium, giving a P/V ratio of 1.6. The P/V ratio of the samples collected over the North Atlantic is 1.25 ± 0.26 (Table 7). Based on the limited data on P/V ratios in combustion emissions, this ratio suggests that both coal and fuel oil particulates are present in the samples. The presence of coal fly ash and oil soot in the air over the North Atlantic in the temperate zone has been well documented (Folger, 1970; Parkin et al., 1970). Parkin et al. (1970) found pollution particles to be between 3 and 27% of the total particles in the open ocean and to actually outnumber those from natural sources in the Bay of Maine.

Linton et al. (1976) have also measured the phosphorus concentration on the surface of flyash particles with an electron microprobe. They found the phosphorus concentration on the surface to be 3.8 times greater than the bulk concentration. Surface vanadium concentrations were found to be twice as high as in the interior. The surface P/V ratio is therefore about 3. The surface enrichment of phosphorus on fly ash particles may provide an explanation for the distribution of excess vanadium - associated phosphorus between the reactive and AS+O fractions. It may be that the phosphorus on the surface of the fly ash particle is readily soluble in water, while the phosphorus contained in the interior of the particle is not.

From Air Mass Trajectories

The trajectories of air masses sampled on Cruises 161 and 168 were calculated from 700 mb pressure charts for the appropriate dates. Starting at the midpoint longitude and latitude of sample collection, trajectories were traced backwards in time until the point of landfall and source region was readily apparent. Pressure charts are available at 12 hour intervals, a separate trajectory was calculated every 12 hours for each sample. As sampling times varied, more trajectories were calculated for some samples than for others.

Trajectories for four samples are presented here along with their chemical analyses to illustrate the relationship between air mass source and aerosol composition. Figs. 3 and 4 show trajectories for two samples taken in a similar location in the North Atlantic in December 1974 and in June 1975. Air flow in the winter period is basically from Mexico across the Gulf, over Florida, and into the Atlantic. In the summer, when the Bermuda high has moved northwards, the air in this part of the Atlantic appears to come more typically from the Caribbean passing over Cuba and southern Florida. Aluminum values are similar at both times of the year, but sodium and vanadium values are higher in the winter samples. Seas are normally rougher in the winter; the average wind speed during the collection of the winter sample was 5.5 m s^{-1} vs 3.8 m s^{-1} for the period of collection of the summer sample. The excess vanadium concentration is twice as high in the winter samples. Even in the southern United States, a significant amount of vanadium is injected into the atmosphere from fossil fuel combustion. The higher phosphorus

Fig. 3 Air mass trajectories of Sample 7,
cruise TR 161, December 1974.

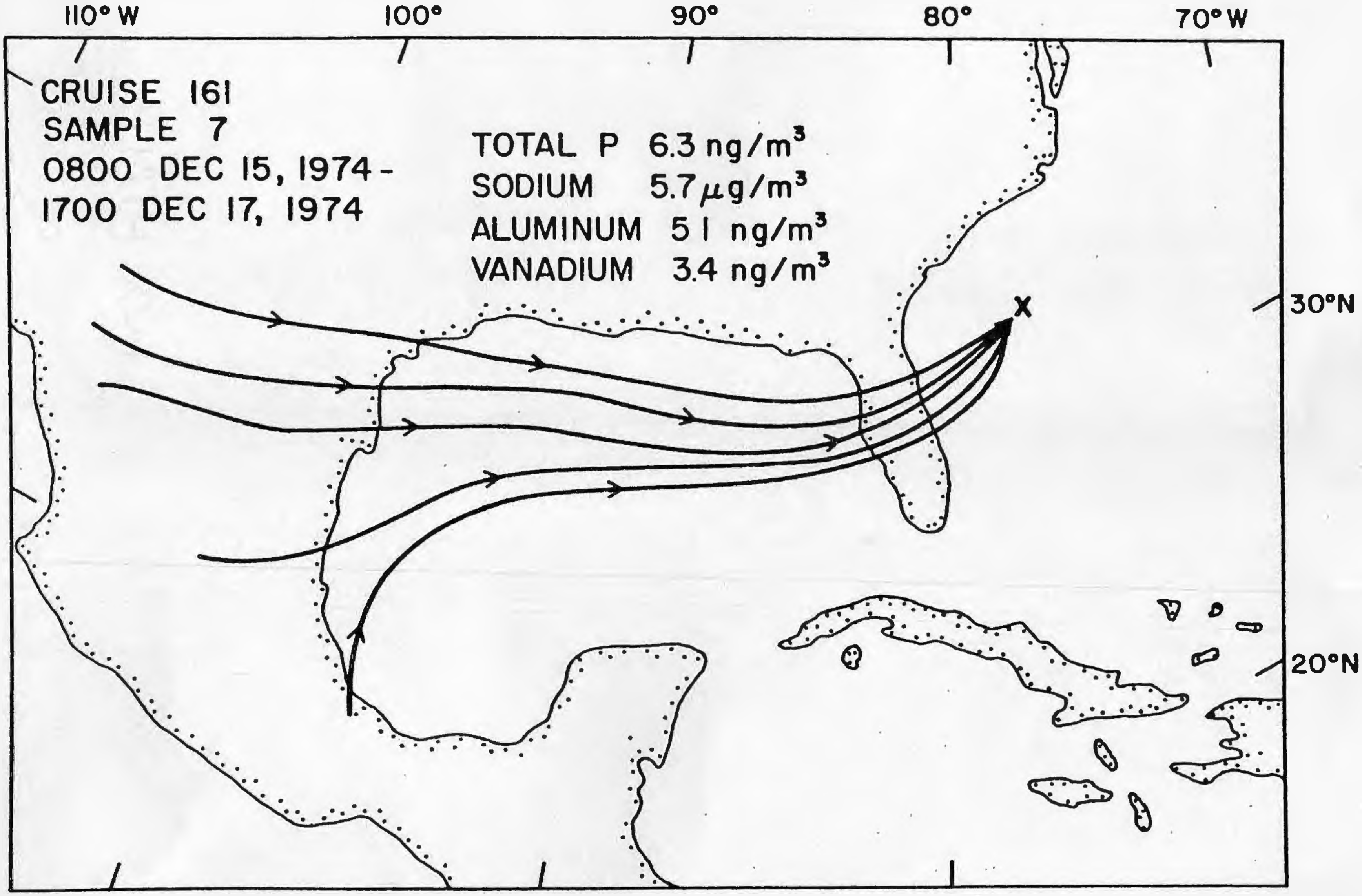
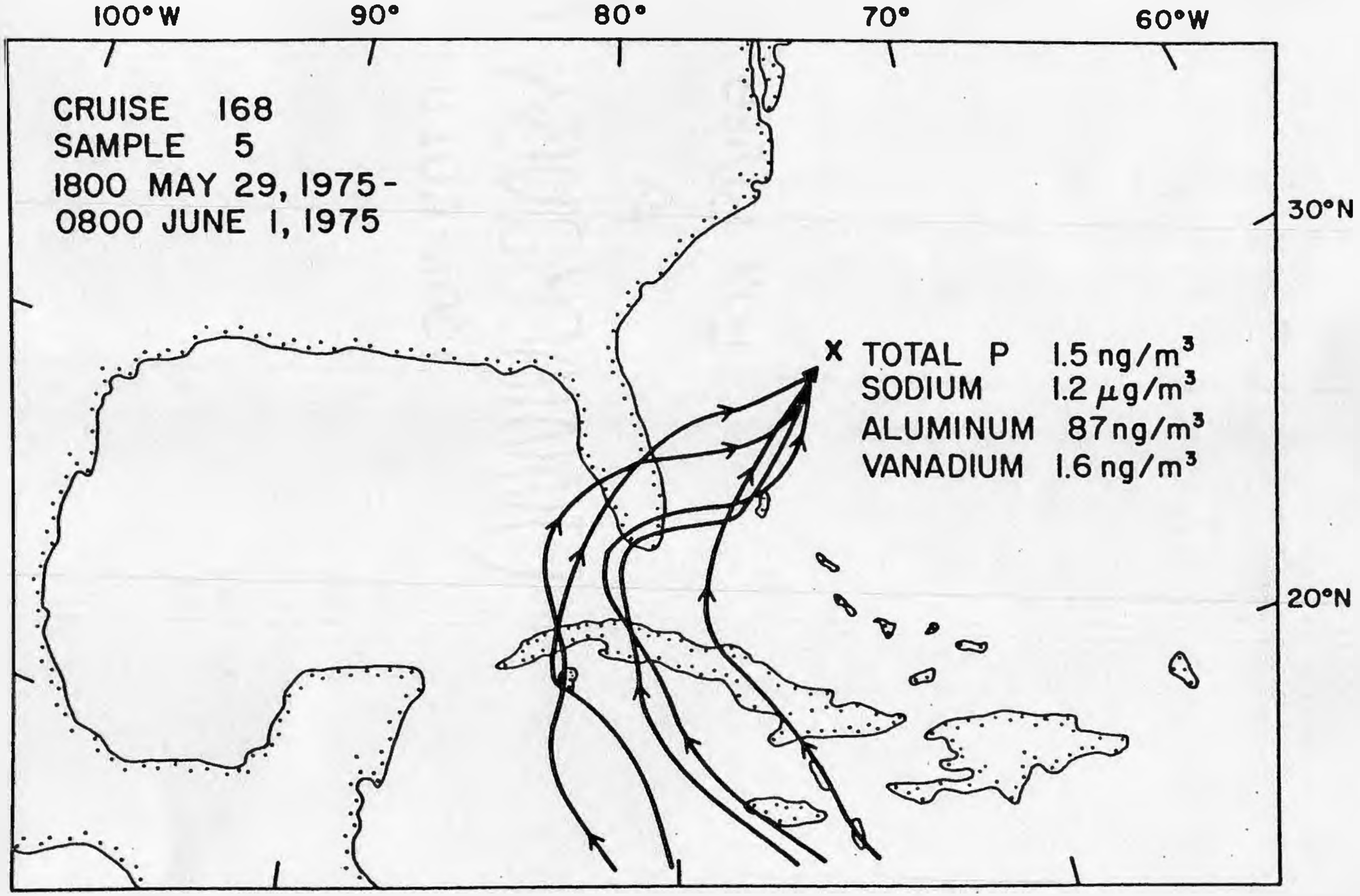

110° W
100°
90°
80°
70° W
30°N
20°N
CRUISE 161
SAMPLE 7
0800 DEC 15, 1974 -
1700 DEC 17, 1974
TOTAL P 6.3 ng/m³
SODIUM 5.7 μg/m³
ALUMINUM 51 ng/m³
VANADIUM 3.4 ng/m³
X

Fig. 4 Air mass trajectories of Sample 5,
cruise TR 168, May 1975.


100° W
90°
80°
70°
60°W
30°N
20°N
CRUISE 168
SAMPLE 5
1800 MAY 29, 1975-
0800 JUNE 1, 1975
X
TOTAL P 1.5 ng/m^3
SODIUM 1.2 μg/m^3
ALUMINUM 87 ng/m^3
VANADIUM 1.6 ng/m^3

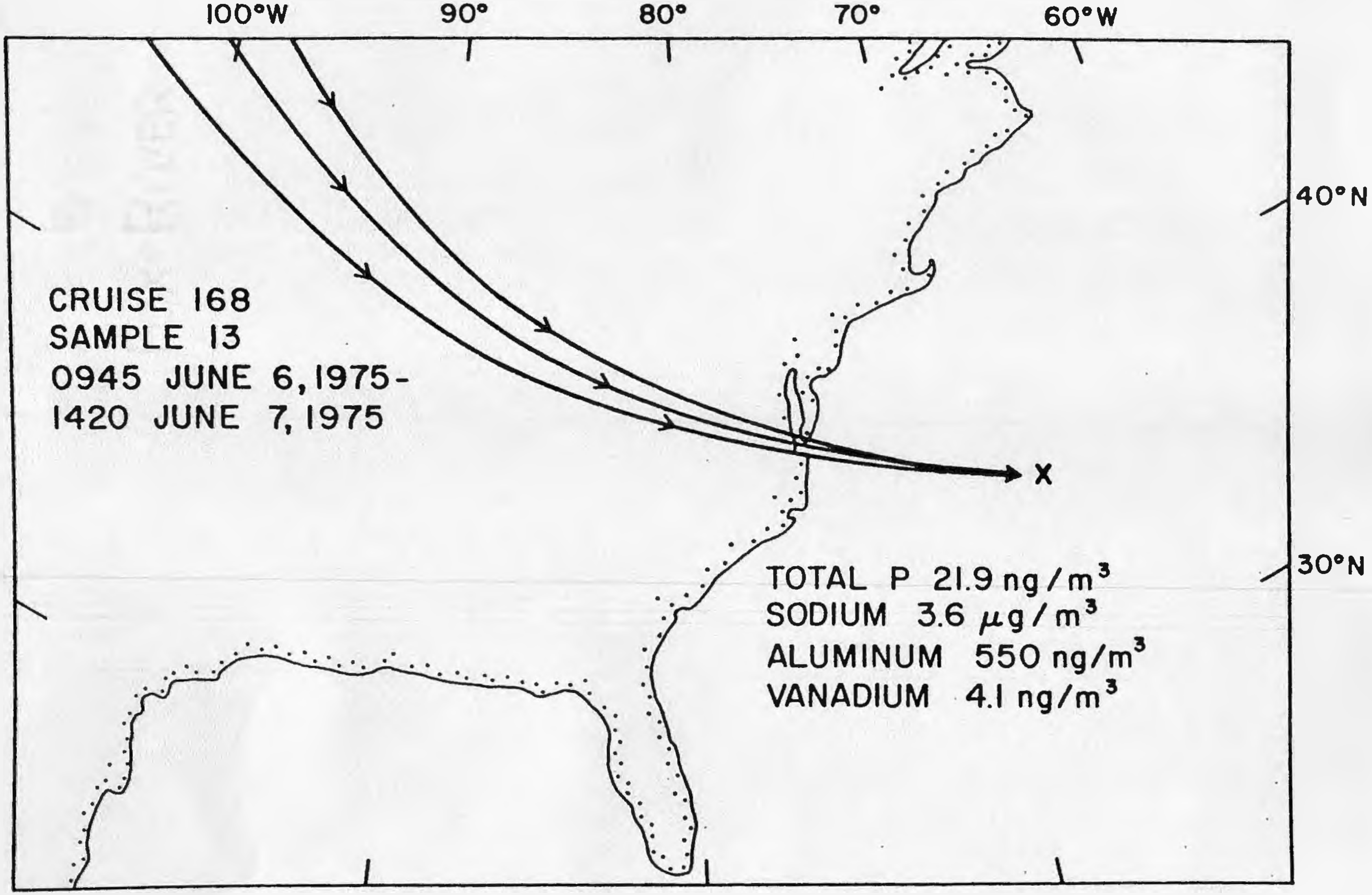
concentration in the winter sample can then be attributed to both greater amounts of sea salt and anthropogenic particulates in the atmosphere at that time.

Fig. 5 illustrates a summer sample collected off the coast of Cape Hatteras. The air masses sampled at this particular location had passed over the midwestern and middle Atlantic states before moving offshore. The concentrations of both crustal and anthropogenic material are high, with subsequently high phosphorus content.

The sample illustrated in Fig. 6 contained a relatively large amount of phosphorus and excess vanadium compared to the other samples. Sea-salt sodium and crustal aluminum, on the other hand, were fairly low in concentration. Thus it appears that the high phosphorus concentration found in this sample may be due to the presence of particulates from fossil fuel combustion processes. The presence of these combustion products is indicated by the relatively high excess vanadium concentration. Vanadium concentrations in the northeast are often extremely high due to the large quantities of high vanadium residual fuel oil burned in this region (Zoller et al., 1973). Concentrations in the Boston area range from 400-2000 ng m^{-3} (Zoller and Gordon, 1970). Fig. 6 shows that the air masses sampled passed directly over New England.

Air mass trajectories are also available during the time that samples were collected at Bermuda. The computer calculated trajectories were supplied to me by the staff of the NOAA "Geophysical Monitoring for Climatic Change" program. The six-hourly near-surface (300 to 1200 m) trajectories were computed using the Regional-Continental Scale Trajectory Program described by Heffter et al. (1975). Samples were collected for periods ranging from 4 to 7 days, thus 16 to 28 separate

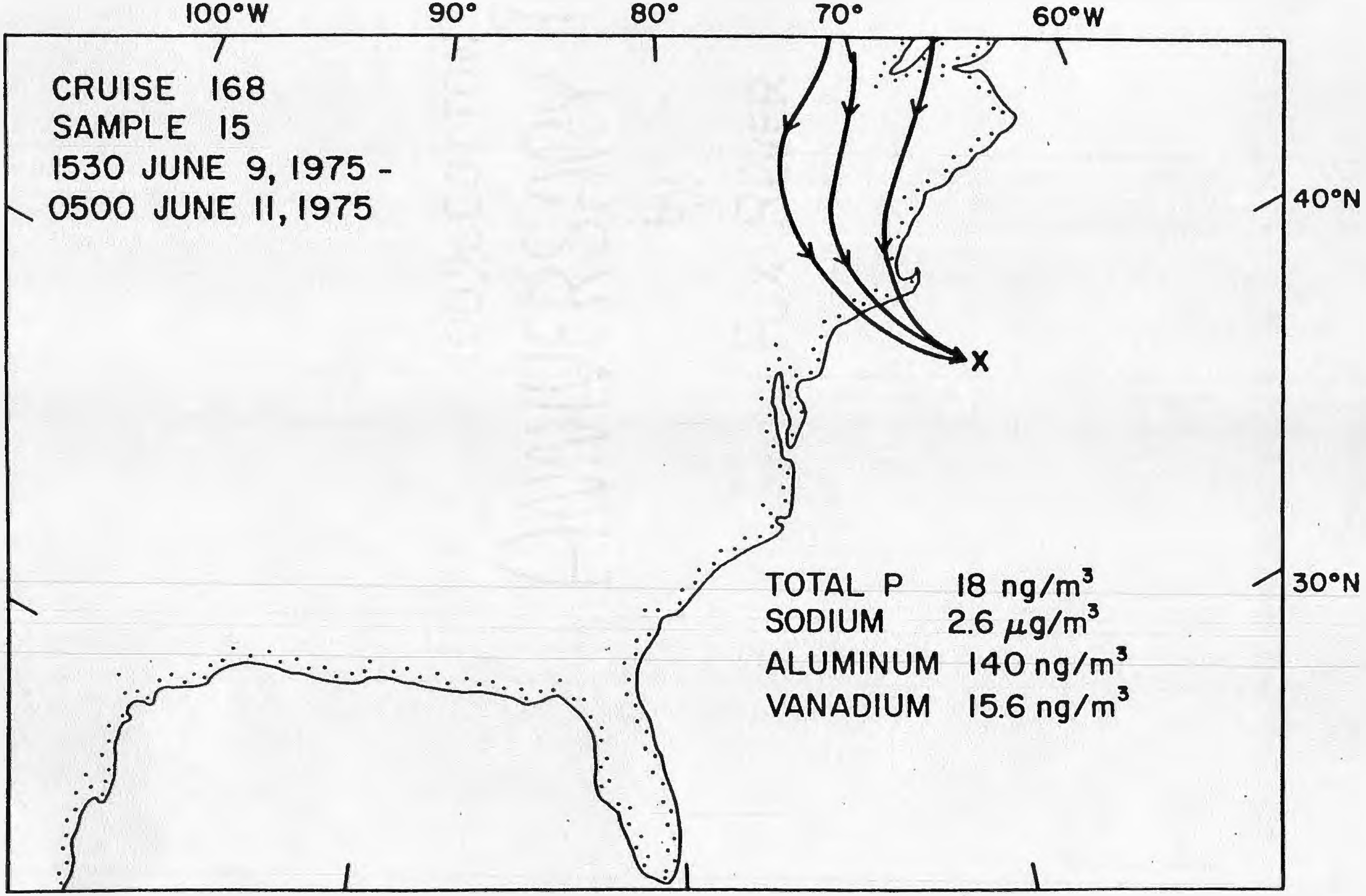
Fig. 5 Air mass trajectories of Sample 13, cruise TR 168, June 1975.



CRUISE 168
SAMPLE 13
0945 JUNE 6, 1975-
1420 JUNE 7, 1975

TOTAL P 21.9 ng / m^3
SODIUM 3.6 μg / m^3
ALUMINUM 550 ng/m^3
VANADIUM 4.1 ng/m^3

Fig. 6 Air mass trajectories of Sample 15,
cruise TR 168, June 1975.


100°W
90°
80°
70°
60°W
40°N
30°N
CRUISE 168
SAMPLE 15
1530 JUNE 9, 1975 -
0500 JUNE 11, 1975
X
TOTAL P 18 ng/m³
SODIUM 2.6 µg/m³
ALUMINUM 140 ng/m³
VANADIUM 15.6 ng/m³

trajectories were available for each Bermuda sample. Because most samples were exposed to air masses from several sources, a weighted average trajectory number was calculated for each sample. Basically, the compass was divided in four sectors as shown in Fig. 7.

Air masses arriving from Sector 1 should be representative of uncontaminated marine air. Those arriving from Sector 2 have passed over the islands of the Caribbean and also may, when the Bermuda high is in the right location, contain particulate matter carried across the Atlantic from the Sahara desert (Bricker and Prospero, 1969). Air masses arriving in Sector 3 have left the coast of North America between Florida and Cape Hatteras, while those arriving in Sector 4 have passed over the highly populated and industrialized region north of Cape Hatteras. These air masses would be expected to contain significant particulate matter from anthropogenic sources. Trajectories were assigned a value of from 1 to 4 depending on their source region. A sample with 4 trajectories from Sector 3 and 4 from Sector 4 has an average trajectory number of 3.5.

In Figs. 8, 9, and 10, total phosphorus, reactive phosphorus, AS+O phosphorus, sodium, aluminum, and excess vanadium are plotted against trajectory number. High excess vanadium concentrations are strongly associated with air masses from the north and west, i.e., from North America. For excess vanadium the correlation coefficient is 0.72 with a probability (P) of having a true value of zero of 0.03. Sodium, on the other hand, shows little correlation with trajectory number as would be expected from an element with a marine source ($r = 0.23$, $P = 0.55$). Aluminum shows an intermediate behavior ($r = 0.55$, $P = 0.15$) due perhaps to the possibility of crustal material being carried to Bermuda not only

Fig. 7 Source sectors for air masses arriving at Bermuda.

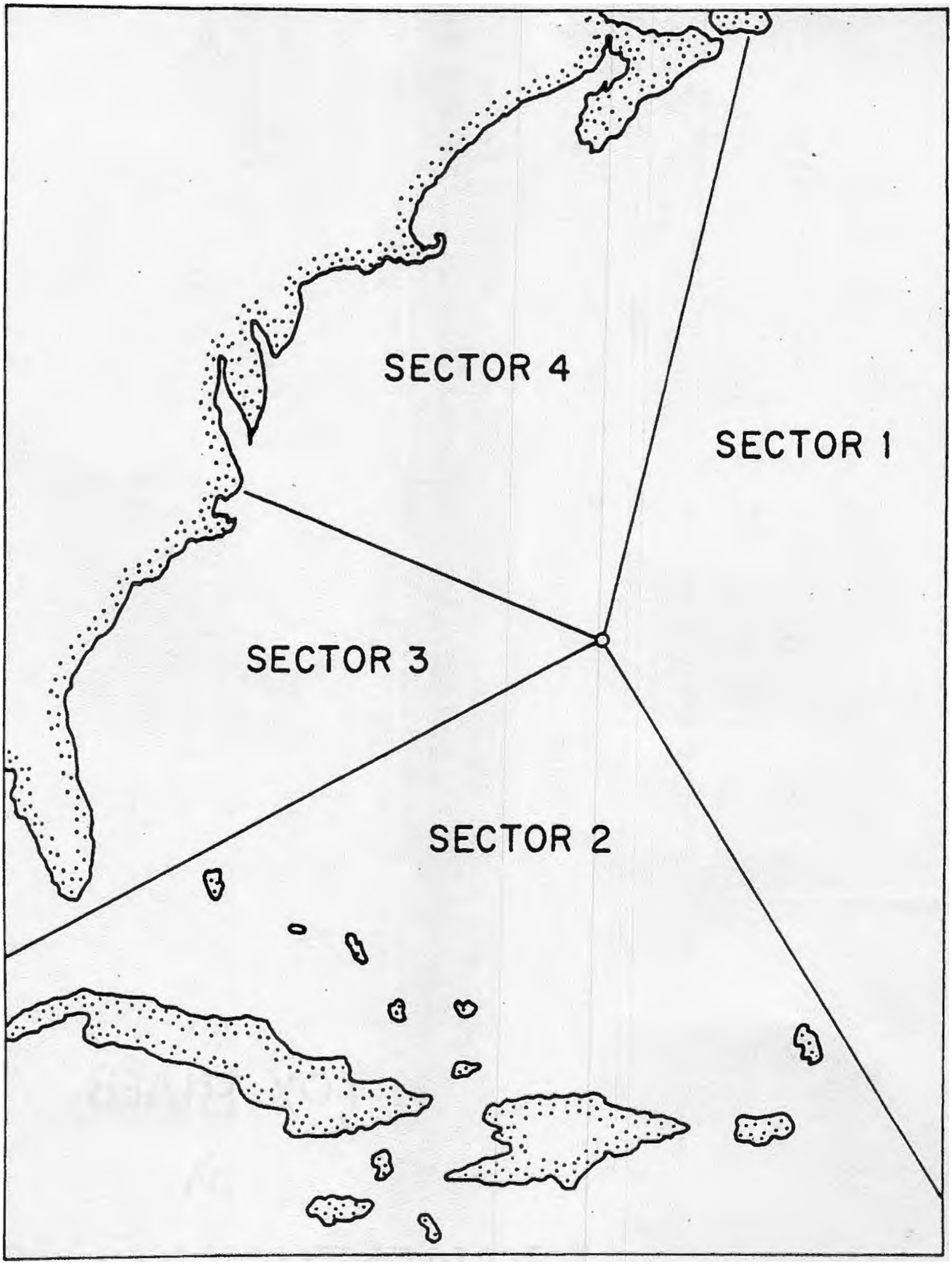

SECTOR 4
SECTOR 1
SECTOR 3
SECTOR 2

Fig. 8 Total phosphorus and AS+O phosphorus vs. trajectory number

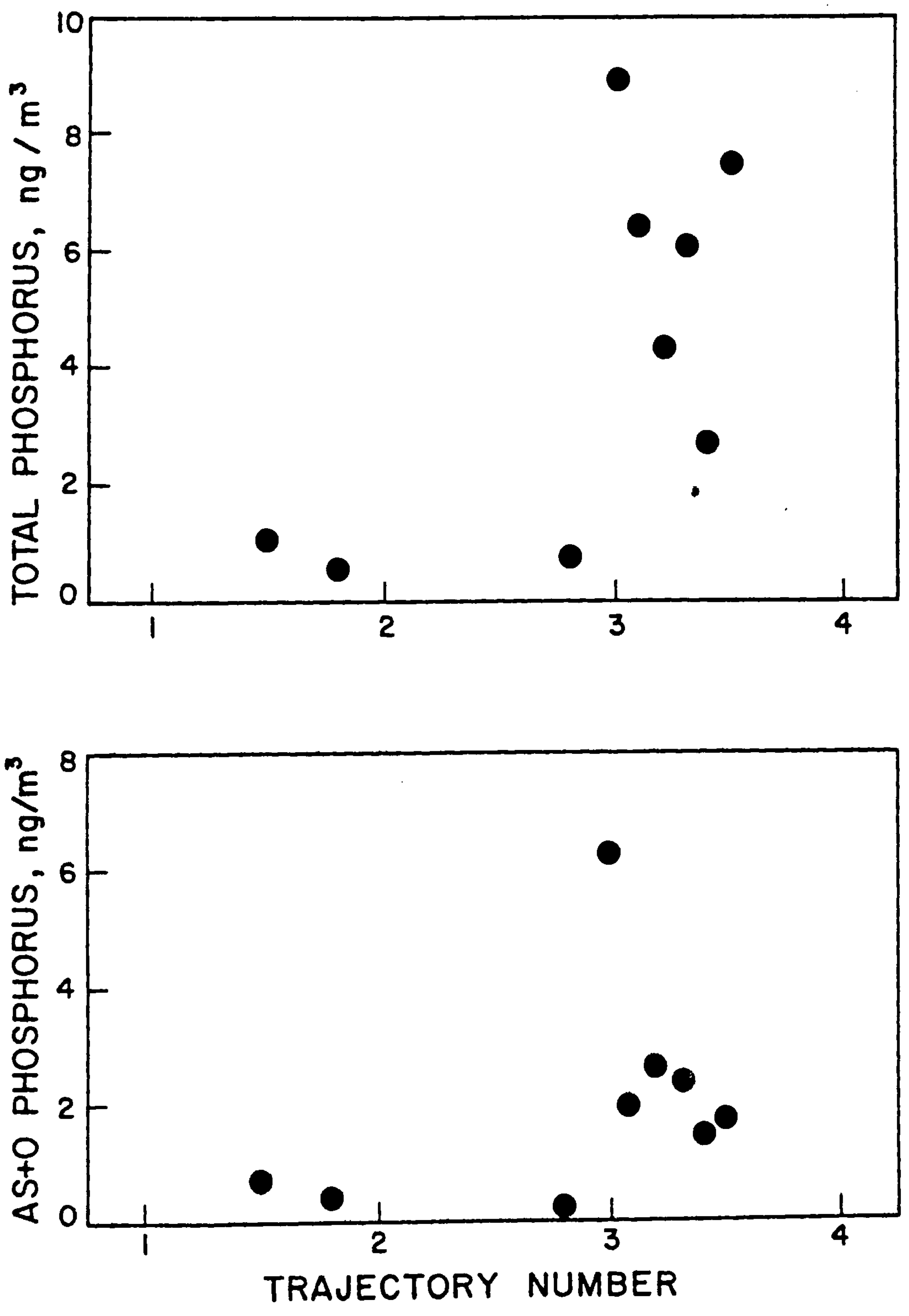
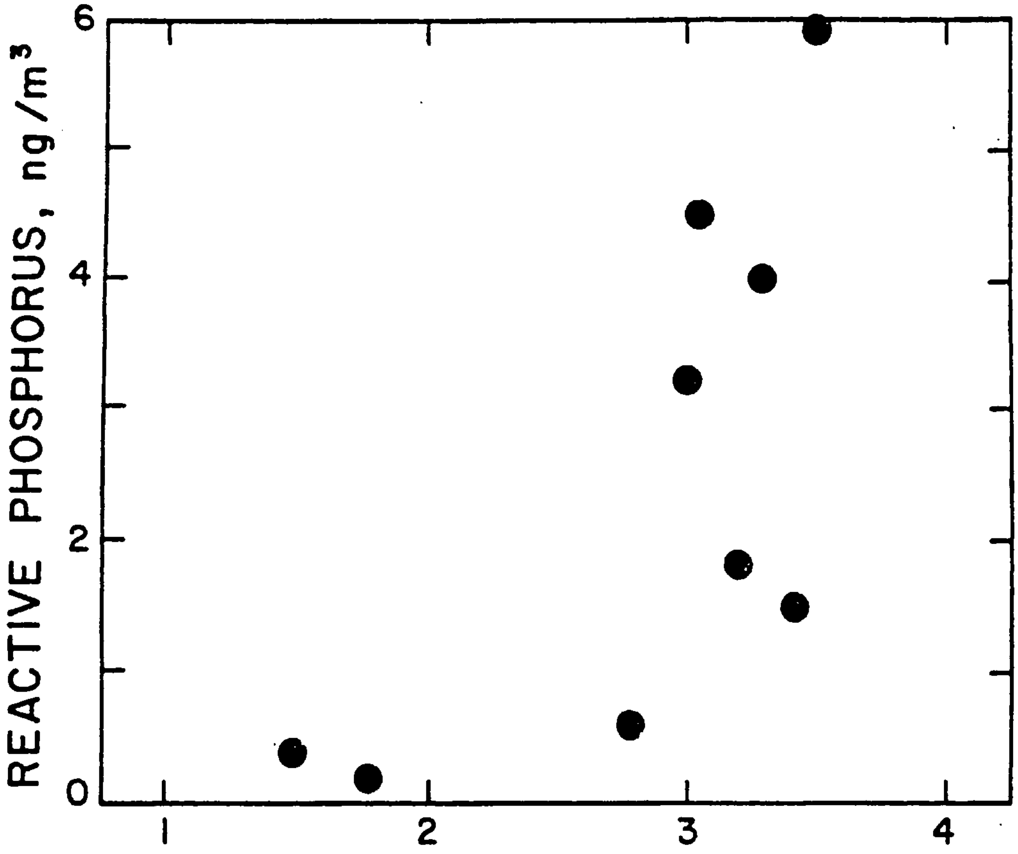

TOTAL PHOSPHORUS, ng / m³
0
2
4
6
8
10
AS+O PHOSPHORUS, ng/m³
0
2
4
6
8
1
2
3
4
TRAJECTORY NUMBER

Fig. 9 Reactive phosphorus and excess vanadium vs trajectory number.


REACTIVE PHOSPHORUS, ng/m³
0
2
4
6
1
2
3
4

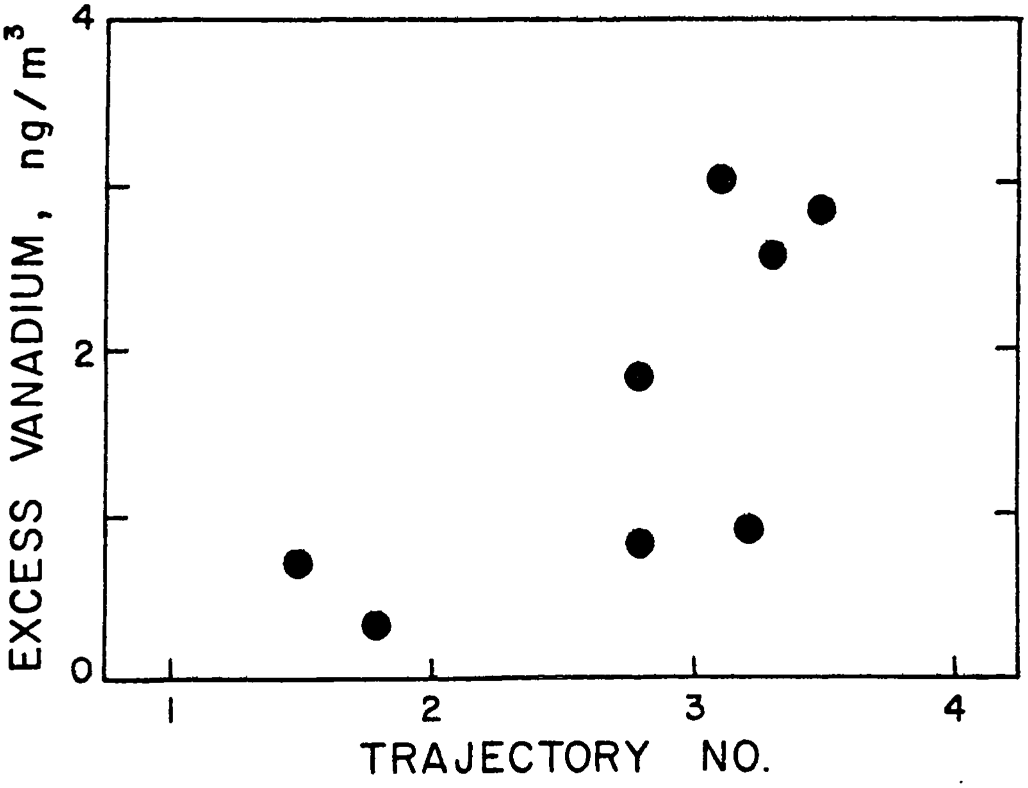
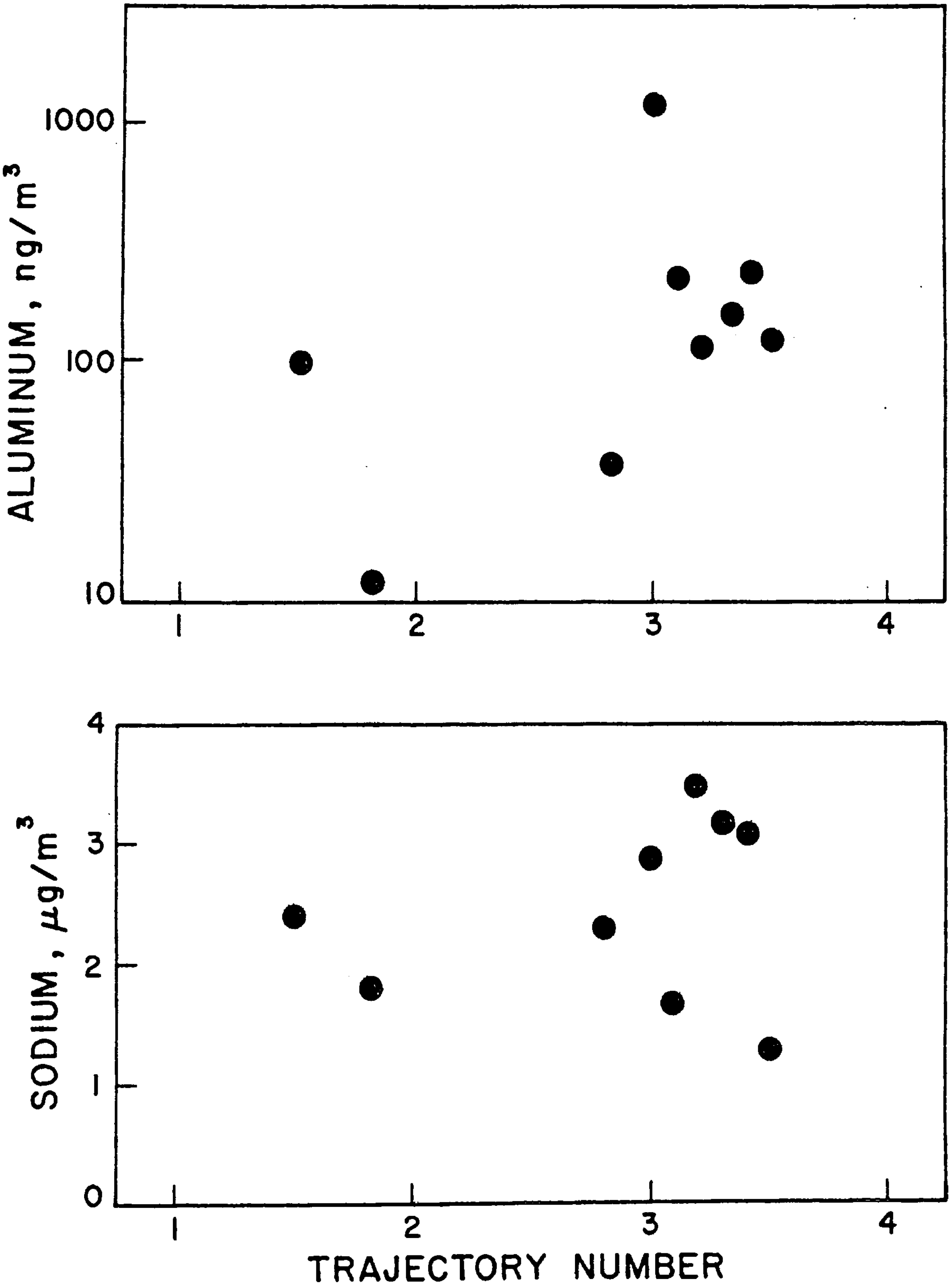

EXCESS VANADIUM, ng/m³
0
2
4
1
2
3
4
TRAJECTORY NO.

Fig. 10 Sea salt sodium and aluminum vs trajectory number.


ALUMINUM, ng/m^3
1000
100
10
1
2
3
4
SODIUM, μg/m^3
4
3
2
1
0
1
2
3
4
TRAJECTORY NUMBER

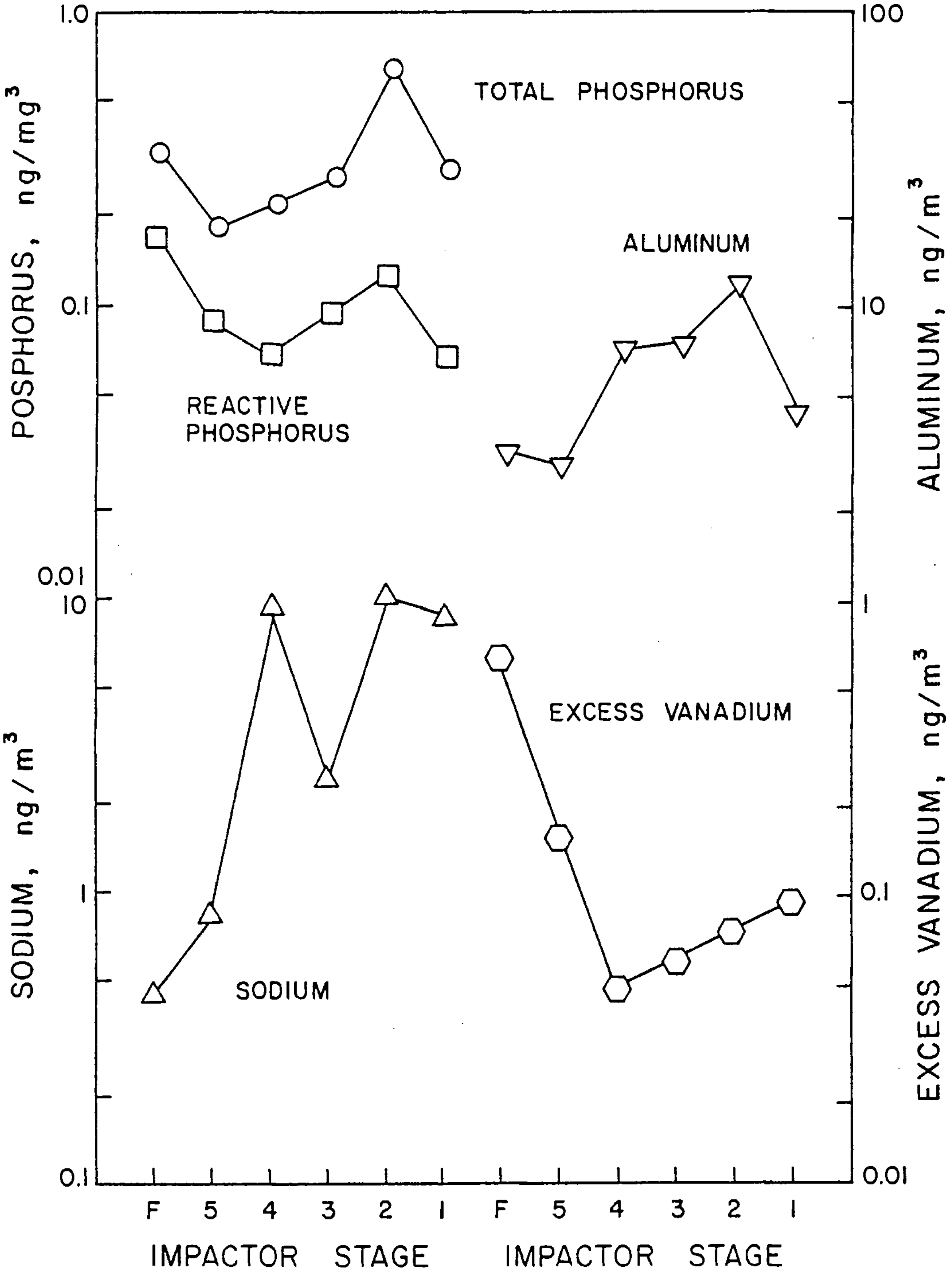
from North America but also from the Sahara Desert of Africa. Bricker and Prospero (1969) suggest that Sahara material can reach Bermuda in the summer months when the Bermuda high has moved northward. One very high aluminum value occurs at trajectory number of 3 (Fig. 11). This sample may contain dust from the Sahara desert, as about one-half the trajectories of the sample are from the SSW in Sector 2, the direction from which Saharan material should approach the island.

The concentrations of reactive phosphorus vary with trajectory number in a manner similar to that of the excess vanadium, suggesting a North American source for most of this material (r = 0.69, P = 0.04). The high value for AS+O phosphorus (Fig. 9) on the other hand, is from the sample that showed the high aluminum concentration. The Sahara aerosol contains mostly water insoluble phosphates; (this thesis. Chap. 3). Thus Sahara material may be the source of the phosphorus in this sample.

From particle size distribution measurements

A Sierra high volume cascade impactor sample was collected at Bermuda in parallel with filter sample #7. The sample has an average trajectory number of 3.4. According to the manufacturer of the impactor, the equivalent aerodynamic radius cutoffs for particles with a density of 1 g cc^{-1} are as follows: Stage 1 = 3.6 μm; Stage 2 = 1.5 μm; Stage 3 = 0.75 μm; Stage 4 = 0.48 μm; Stage 5 = 0.25 μm; backup filter = <0.25 μm. The distribution of sodium, aluminum, excess vanadium, and phosphorus over the stages is shown in Fig. 11. The sodium value for Stage 4 appears to be anomalous when compared to other sodium profiles obtained at this site (Duce et al., 1976). The total and reactive

Fig. 11 Concentration of phosphorus, sodium, aluminum, and excess vanadium vs impactor stage as measured at Bermuda.


1.0
0.1
0.01
10
1
0.1
100
10
1
0.1
0.01
POSPHORUS, ng/mg^3
SODIUM, ng/m^3
ALUMINUM, ng/m^3
EXCESS VANADIUM, ng/m^3
TOTAL PHOSPHORUS
REACTIVE PHOSPHORUS
ALUMINUM
SODIUM
EXCESS VANADIUM
F 5 4 3 2 1
F 5 4 3 2 1
IMPACTOR STAGE
IMPACTOR STAGE

phosphorus distributions show a peak at Stage 2. Material of crustal or sea salt origin is usually on this stage. However there also appears to be a significant amount of phosphorus on the final filter. The bulk of the excess vanadium is also found on the backup filter. I believe that these distributions provide additional evidence for the presence over the North Atlantic of relatively large amounts of phosphorus from anthropogenic industrial sources.

TRANSPORT OF PHOSPHORUS TO THE WESTERN NORTH ATLANTIC

I calculate the transport of phosphorus from the North American continent in three ways. In my first calculation I estimate the amount of phosphorus transported over the coast of North America between 25 and 45°N. This is a linear distance of approximately 2200 Km. I assume from Fig. 2 a phosphorus concentration at the coast of 10 ng m^{-3} between 25 and 35°N and 20 ng m^{-3} between 35°N and 45°N. Based on the measurements of Gillette and Blifford (1971) and of Shaw (1975) I assume a scale height for particulate phosphorus of 1.5 Km between 1 and 4 Km. I assume constant concentration above 4 Km to the tropopause.

The average time for 160 air masses computed for 1974 and 1975 to travel between the North American coast above 35°N and Bermuda was 88 h, for an average velocity of 3.9 m s^{-1} over the approximately 1200 Km of distance. Ninety-three air masses which left the coast below 35°N took an average of 103 h and thus averaged 3.7 m s^{-1} over approximately 1400 Km. I assume a 3.8 m s^{-1} average velocity for air masses leaving the North American continent. The resulting flux of phosphorus is approximately 7.5×10^9g y^{-1}.

My second approach is to estimate a deposition velocity from the regression curves shown in Fig. 2. Assuming an exponential decrease in phosphorus concentration with increasing distance from the coast, I estimate the deposition velocity from the equation

$$\ln C/C_o = H/V_t \cdot t$$

where C is the final concentration, C_o is the initial concentration, H is the height of the mixing layer, t is the transit time in hours, and V_t is the total deposition velocity. V_t includes deposition due to rainout, washout, and dry fallout (Junge, 1963). Implicit in the use of this equation is the assumption that all of the decrease in phosphorus is due to deposition onto the ocean surface. I assume H to be 2000 m. Above Cape Hatteras, I use C_o as 20.5 ng m^{-3} at the coast and 9.8 ng m^{-3} at Bermuda, with a transit time of 88 h. Below Cape Hatteras the values are 9.9 nm^{-3}, 1.0 ng m^{-3}, and 103 h respectively. Deposition velocities are then calculated to be 0.4 ± 0.2 cm s^{-1} for the northern sector and 1.2 ± 0.5 cm s^{-1} in the southern sector. The lower deposition velocity calculated for the northern sector suggests that the phosphorus is contained in smaller particles in this sector. This result is in good agreement with results of the trajectory studies of the Bermuda samples and of the analysis of the cascade impactor sample collected at Bermuda. These data also suggest that much of the phosphorus from the northeastern coast of North America is contained in small particles most likely of industrial origin.

The average concentration of total particulate phosphorus in the marine air over the northern sector is ∿11 ng m^{-3}, while the average concentration over the southern sector is ∿5 ng m^{-3}. The area of the North Atlantic sampled in this study is roughly a triangle bounded by the North American coast, a line along 25°N latitude, and a line along 65°W longitude. The total area of this triangle is roughly 2.5 x 10^6 Km^2, about 1.5 x 10^6 Km^2 is in the southern sector while 1.0 x 10^6 Km^2 lies in the northern sector.

Using the deposition velocities, phosphorus concentrations, and areas for each sector, the annual phosphorus deposition to the whole triangle is estimated to be 4×10^{9} g.

The final estimate is obtained by simply applying the deposition rate of 0.06 Kg ha y^{-1} measured at Bermuda to the area of 2.5×10^{6} Km^{2}. An annual deposition of 1.5×10^{10}g y^{-1} is calculated. Approximately 30% of the explicable variance of total phosphorus is explained by the regression with sea-salt sodium (Table 7). Thus I assume that 30% of the calculated deposition to the ocean is recycled marine material. The net addition to the oceans then is about 1×10^{10}g y^{-1}.

Considering the necessary approximations involved in these calculations, the agreement between the three approaches is reasonably good. The total depsition samples collected on Bermuda may include Sahara material along with that from North America. Thus this estimate based on the deposition rate at Bermuda may overstate the flux from North America. The calculation based on deposition velocities may also overstate the phosphorus flux, as no allowance is made for simple dilution of the continental air masses by marine air masses of lower phosphorus content. However, the two calculations do bracket the estimate of phosphorus transported over the North American coast. This suggests that the bulk of the phosphorus in air masses from North America is deposited in the western portion of the North Atlantic ocean.

RELEASE IN OCEAN WATER

The exact amount of aerosol phosphorus that will become available as a nutrient upon contact with sea water is difficult to estimate. Availability probably depends on the types of phosphorus present, the size of the aerosol particle, the turbulence of the mixed layer, and the existence in the oceans of such processes as bubble flotation of mineral grains. However, the amount of phosphorus released over a 12 hour period has been determined by extracting 40 aerosol samples collected at Narragansett, Rhode Island, and on cruises TR 145 and TR 168 with low phosphorus (0.1 μM) Sargasso Sea water. Samples were extracted for 12 hours in the dark and then analyzed for reactive phosphorus. It was found that an average of 36 ± 15% of the total phosphorus was released over a 12 hour period. Based on this percentage, I estimate that 2 to 4×10^9 gms of nutrient phosphorus are added annually to the western North Atlantic between 25 and 45°N. Riverine input from the east coast of North America has been estimated to be about 5×10^{14} l y^{-1} (Judson and Ritter, 1964). Using an average total phosphorus content of 60 μg l^{-1} for phosphorus in rivers (Stumm, 1973), I calculate 3×10^{10} g y^{-1} of phosphorus is added to the western North Atlantic. The atmospheric input of nutrient phosphorus thus amounts to about 10% of the riverine input. However, the riverine input is added to estuaries and coastal waters, while atmospheric deposition occurs over a wide area, including much of the nutrient poor Sargasso Sea. Thus the atmosphere may be a more important source of nutrient phosphorus to open ocean regions than the gross figures would indicate.

ACKNOWLEDGEMENTS

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THE SEA AS A SOURCE OF ATMOSPHERIC PHOSPHORUS

ABSTRACT

The geochemical fractionation of phosphorus on the drops from bubbles bursting in sea water has been studied using a field sampler called the Bubble Interfacial Microlayer Sampler (BIMS). The droplets from bursting bubbles were collected on filter samples in Narragansett Bay, Rhode Island during the summer of 1975. Phosphorus was found to be fractionated by the bubble bursting process. The enrichment factor ranged from 4 to 170. Enrichment was found to increase with decreasing surface water phosphorus concentration while it decreased with increasing wind velocity. Enrichment was independent of bubbling depth. Together these facts suggest that the sea-surface microlayer is the source of the phosphorus on the ejected drops. Organic phosphorus on the filter samples was found to be enriched relative to surface water phosphorus by factors of 100-200, while reactive phosphorus was enriched by factors of only 6-8. This suggests that surface-active organic phosphorus compounds are the source phosphorus in the microlayer.

The organic phosphorus content of samples of atmospheric particulates collected over the phosphate-rich upwelling waters near the Peru coast was found to correlate significantly with sea-salt sodium. Enrichments calculated using the average phosphorus concentration of the surface water in this area agree well with the results of the BIMS study. Thus it appears that phosphorus fractionation does occur in nature and may be important in supplying this nutrient to some coastal regions of the world. No evidence, however, was found for the conversion of dissolved reactive phosphorus to particulate organic phosphorus by the action of bursting bubbles.

INTRODUCTION

Sea salt particles comprise a major fraction of atmospheric particulate matter (Robinson and Robins, 1971). The estimated annual production rate of sea salt particles of radii less than 40 μm is between 10^{15} and 10^{16} g yr^{-1}, of which ∿90% is redeposited into the oceans while ∿10% is transported to the continents (Eriksson, 1959, 1960; Blanchard, 1963). Sea salt particles have been shown to have a major influence upon the precipitation chemistry of continental coastal areas (Emaneulsson et al., 1954; Junge and Werby, 1958; Whitehead and Feth, 1964) and of islands (Miller, 1961). The early speculations that sea salt particles can penetrate far inland (Moore and Browning, 1921) have been confirmed by measurements over the inland United States by Crozier et al.(1952) and Byers et al.(1955).

Sea water contains all of the necessary plant macronutrients and so the flux of sea salt to the land has been of interest to investigators studying the atmospheric input of nutrients to terrestrial vegetation. Many of the early analyses of rainwater at coastal stations showed K/Na ratios higher than would be expected if sea water were the source of these elements (Junge, 1963). About this time Wilson (1959) reported on a study of the snows of New Zealand above the vegetation line. Wilson found, in the snow, a correlation between excess K (the amount present above the amount expected based on the sea water K/Na ratio) and albuminoid nitrogen. He further found that a sample of ocean foam contained excess K and albuminoid nitrogen in the same ratio as in the snow samples. The author hypothesized that both K and N had been concentrated at the sea surface microlayer by biological activity, then injected into the atmosphere on sea salt particles by the bursting bubble mechanisms studied by Kientzler et al. (1954) and MacIntyre (1965, 1968).

While some geochemical fractionation processes have been inferred from the analysis of precipitation and particulate aerosol samples, and while small scale laboratory studies have shown that fractionation of some elements should be possible; demonstrating that it does in fact occur in nature has proven to be more difficult. Recent studies (Hoffman and Duce, 1972; Hoffman et al., 1974) indicate that fractionation of potassium does not occur to any degree over the bulk of the ocean surface. While it may well occur in local highly productive areas (Buat-Menard et al., 1974), other reasons must be found for the K/Na ratios found in most precipitation samples.

Hoffman and Duce (1976) showed in a laboratory study that organic carbon is ejected on sea salt particles with a higher ratio of OC/Na than the ratio in the source water. Enrichments averaged 250 when productive Narragansett Bay water was bubbled and 73 when Sargasso Sea water of very low productivity was used. However, the analysis of aerosol samples collected to date in the marine atmosphere in remote areas (Hoffman and Duce, 1974; Hoffman and Duce, 1977) has not shown any correlation between amounts of organic carbon and sea salt on the filters.

The organic carbon concentration was relatively constant over a wide range of sodium concentrations. The organic carbon appears to be present on particles much smaller than those found in the usual sea salt size range (Hoffman and Duce, 1977). Thus while laboratory studies suggest that organic carbon should be present in the marine aerosol and should show considerable enrichment on sea salt particles, this process has not yet been detected in field sampling programs.

Piotrowicz (1977) has investigated the fractionation of Fe, Cu, and Zn in the field using an "in situ" sampler named the Bubble Interfacial

Microlayer Samplers (BIMS). The study, carried out in Narragansett Bay, Rhode Island, found average enrichments of 72 for Fe, 200 for Cu, and 190 for Zn on bubble produced sea salt particles generated by the BIMS. Using factor analysis Duce et al. (1976) have evaluated the concentrations of 12 elements determined on 60 aerosol samples collected at Bermuda in 1973. About 9% of the variation in Fe and 33% of the variation in Zn are associated with the factor which contains the bulk of the Na, Mg, Cu, and K variations and is thought to be the large particle sea salt aerosol. Thus there is some evidence supporting an oceanic input of these two metals. Whether the fractionations measured for these metals with the BIMS are typical of that occurring in the oceans has not yet been determined, however.

The fractionation of phosphorus compounds in sea water was first studied by Baylor et al. (1962) and Sutcliffe et al. (1963). These investigators studied the effects of intense bubbling of sea water upon the concentration and distribution of the phosphate present in the source water and in the collected spray droplets. The concentration of total phosphorus in the spray droplets was found to be higher than the initial concentration in the sea water sample, indicating that fractionation was occurring. The concentration of reactive phosphorus remianing in the sea water sample was found to be related to bubbling time by the equation

$$C_t = C_o e^{-kt}$$

where k is a velocity constant which was found to depend on the rate of bubbling.

The most unusual result of those investigations was the finding that phosphorus was evidently converted from dissolved reactive phosphorus to particulate organic phosphorus during the bubbling process. The conversion occurred most noticeably in the spray droplets, but was also found to have occurred in the sea water being bubbled. The concentration of the particulates in the collected spray droplets was great enough to produce noticeable cloudiness of the accumulated fluid. Surface pressure measurements showed that the spray droplets contained significant amounts of surface active material. Sutcliffe et al. (1963) suggested that large organic surface-active molecules adsorb onto bubbles and produce monomolecular films which may be aggregated into particulate organic material. During the formation of these particles considerable amounts of dissolved reactive phosphate are adsorbed, bound, or changed in such a way as to mask or be unreactive to the analytical method of Strickland and Parson (1960).

MacIntyre made a major laboratory investigation of the bubble fractionation of inorganic phosphate using sodium phosphate tagged with ^{32}P and sodium chloride tagged with ^{22}Na (MacIntyre, 1965; MacIntyre and Winchester, 1969). By using a cascade impactor to collect the drops produced by bubbling and by measuring the beta and gamma emissions on each stage, MacIntyre was able to determine enrichment as a function of the particle size of the ejected drop. The observed enrichments were found to be resolvable into two types. The first was a modest enrichment ($\bar{E}$) of 1-10 which was fairly constant over particle radii of 48 μm to 0.75 μm. Superimposed on this, however, was a peak enrichment ($\hat{E}$) which was centered at 15 μm when carefully prepared pure water was used as the test medium. This peak enrichment ranged from 1 to 1,000, depending on experimental conditions. MacIntyre suggested that the peak enrichment was due to the production of film drops by the bursting bubble, while the source of the linear enrichments $\bar{E}$ was the jet drops ejected by the bubble. For sea water, $\hat{E}$ was found to occur on drops of about 6 μm diameter.

The reasons for the shift were not readily apparent. Bubbling runs made with cationic and anionic surfactants added to the test solutions showed that cationic surfactants enhanced the fractionation process, while anionic surfactants suppressed it. These results were consistent with the hypothesis that negatively charged inorganic phosphorus should interact with the positively charged groups on surface active macromolecules. When the surface active macromolecules are adsorbed onto bubble surfaces, the phosphorus is carried along to be ejected on drops when the bubble ruptures at the water surface.

As in the investigations of the fractionation behavior of other elements, field evidence that phosphorus is injected into the atmosphere from the oceans and is fractionated in the process has been lacking until now. The purpose of the study reported in this paper has been:

1. To determine, using a especially designed field sampling device, if phosphorus is fractionated relative to sodium on the droplets ejected by bubbles bursting at the sea surface.

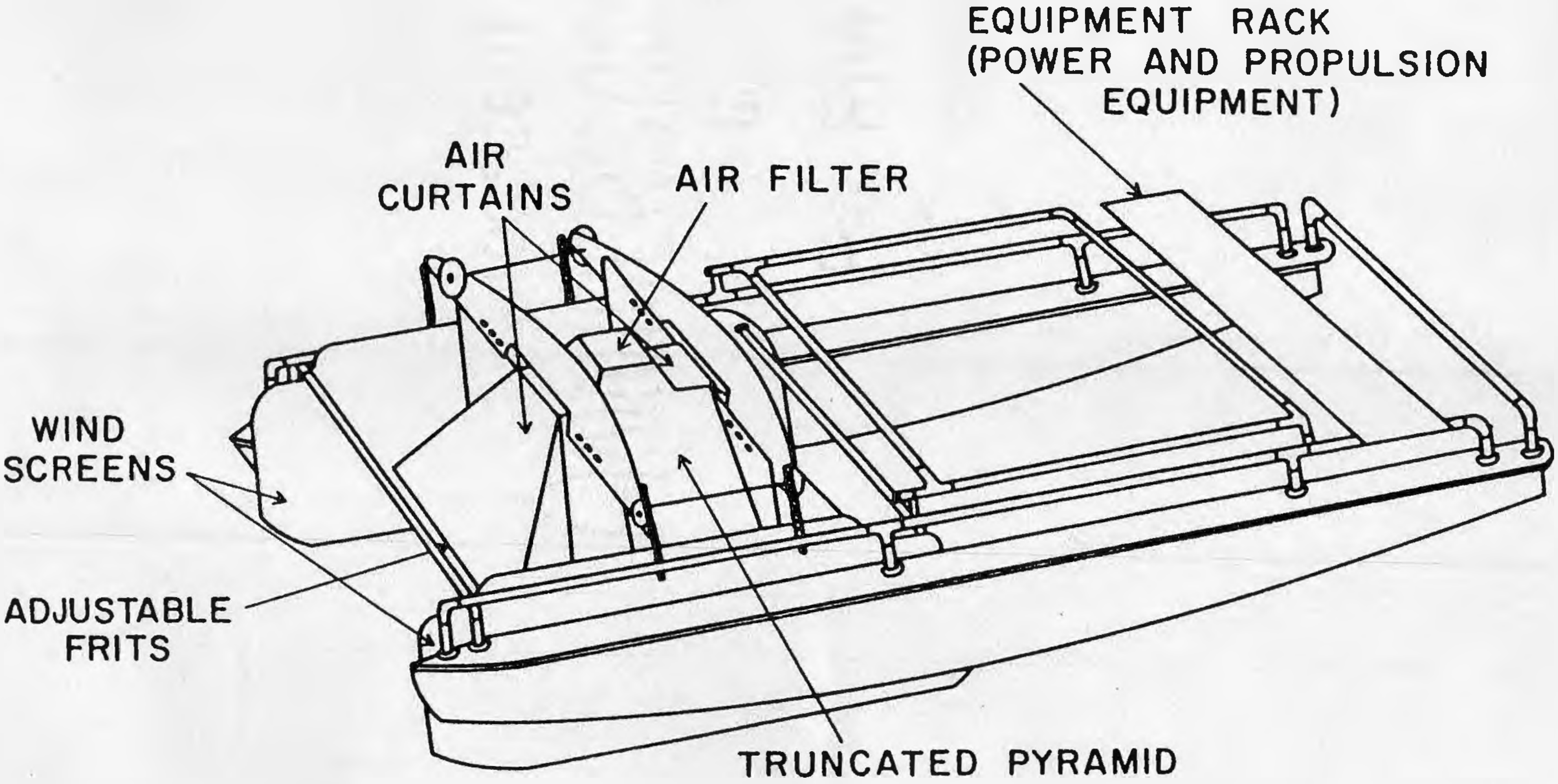
2. To measure the degree of fractionation occurring and to determine if differences in fractionation behavior exist between the organic and inorganic phosphorus fractions of sea water.

3. To search for evidence of naturally occurring fraction of phosphorus by sampling the marine aerosol over waters of high phosphorus content and vigorous bubble action.

BIMS SAMPLING PROGRAM

The Bubble Interfacial Microlayer Sampler (BIMS) was used to carry out a sampling program for phosphorus and trace metals in Narragansett Bay, Rhode Island. The BIMS, shown in Figure 1, is suspended between the

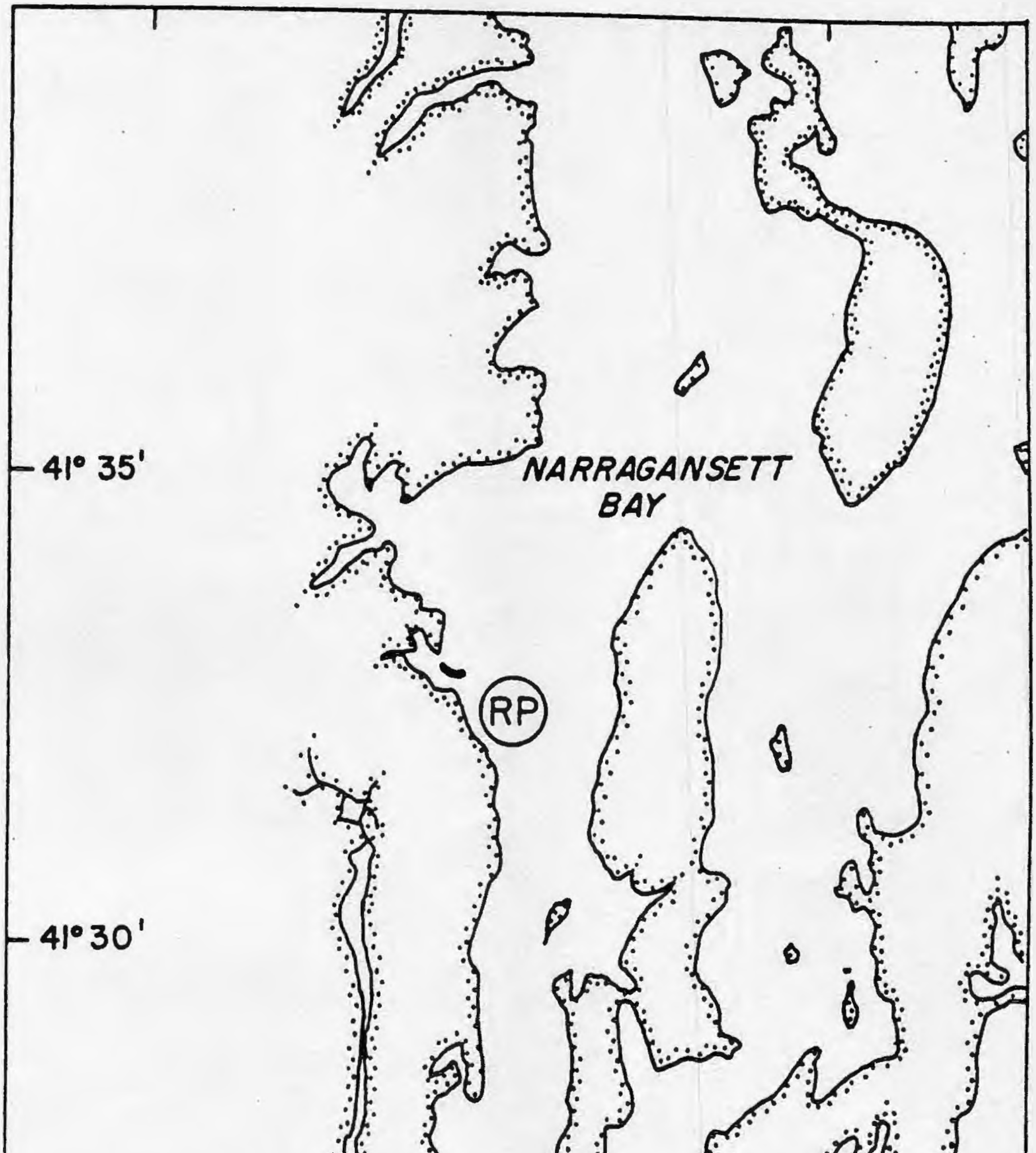
Fig. 1 The Bubble Interfacial Microlayer Sampler


EQUIPMENT RACK (POWER AND PROPULSION EQUIPMENT)
AIR CURTAINS
AIR FILTER
WIND SCREENS
ADJUSTABLE FRITS
TRUNCATED PYRAMID

twin hulls of a 4-meter-long catamaran. It produces bubbles approximately 1000 μm in diameter by forcing compressed nitrogen at a flow rate of approximately 7 l min^{-1} through seven glass frits, 120 mm in diameter, at adjustable depths down to 50 cm beneath the sea surface. These bubbles rise and burst at the sea surface creating jet and film drops in the atmosphere enclosed within the truncated pyramid of the BIMS. The ambient marine atmosphere is excluded from the interior of the BIMS by clean air curtains in the front and back, wind screens on either side, and a slight positive pressure inside. The artificially produced sea salt particles are collected from the enclosed atmosphere at the top of the truncated pyramid on 20 x 25 cm Whatman 41 or Delbag Microsorban 97/99 filters using a commercial high-volume sampling pump. The Delbag filters are reported to be 99% efficient for the removal of particles >0.3 μm in diameter (Daws et al., 1972) while the Whatman 41 filters are reported to be >90% efficient for removing particles >0.25 m in diameter (Stafford and Ettinger, 1972). The exhaust from the pump is filtered through a Delbag filter. This filter offers little resistance to air flow but maintains a high particle efficiency. This air is then recycled back into the BIMS as the air supply for the air curtains. The BIMS has been described in detail by Fasching et al. (1974) and Piotrowicz (1977).

Samples were collected on seven days between May and August, 1975 in the West Passage of Narragansett Bay between Rome Point and Green Point in water 7-15 m in depth. The general sampling area is identified as "RP" in Figure 2. Particles produced by bubbles generated at depths between 2 and 44 cm were sampled over the seven sampling periods. Sampling times ranged from 18 to 45 minutes. Since the air curtains are

Fig. 2 General sampling area of BIMS aerosol samples


41° 35'
41° 30'
NARRAGANSETT BAY
RP
RHODE ISLAND SOUND
71°30'
71°20'

not 100% efficient, at least one and sometimes two curtain blanks were collected each sampling day by collecting a sample with the air curtains running but without the bubbler in operation. The analytical results for each day's samples are corrected by this curtain blank. Details of the BIMS operating procedure have been given in Piotrowicz (1977).

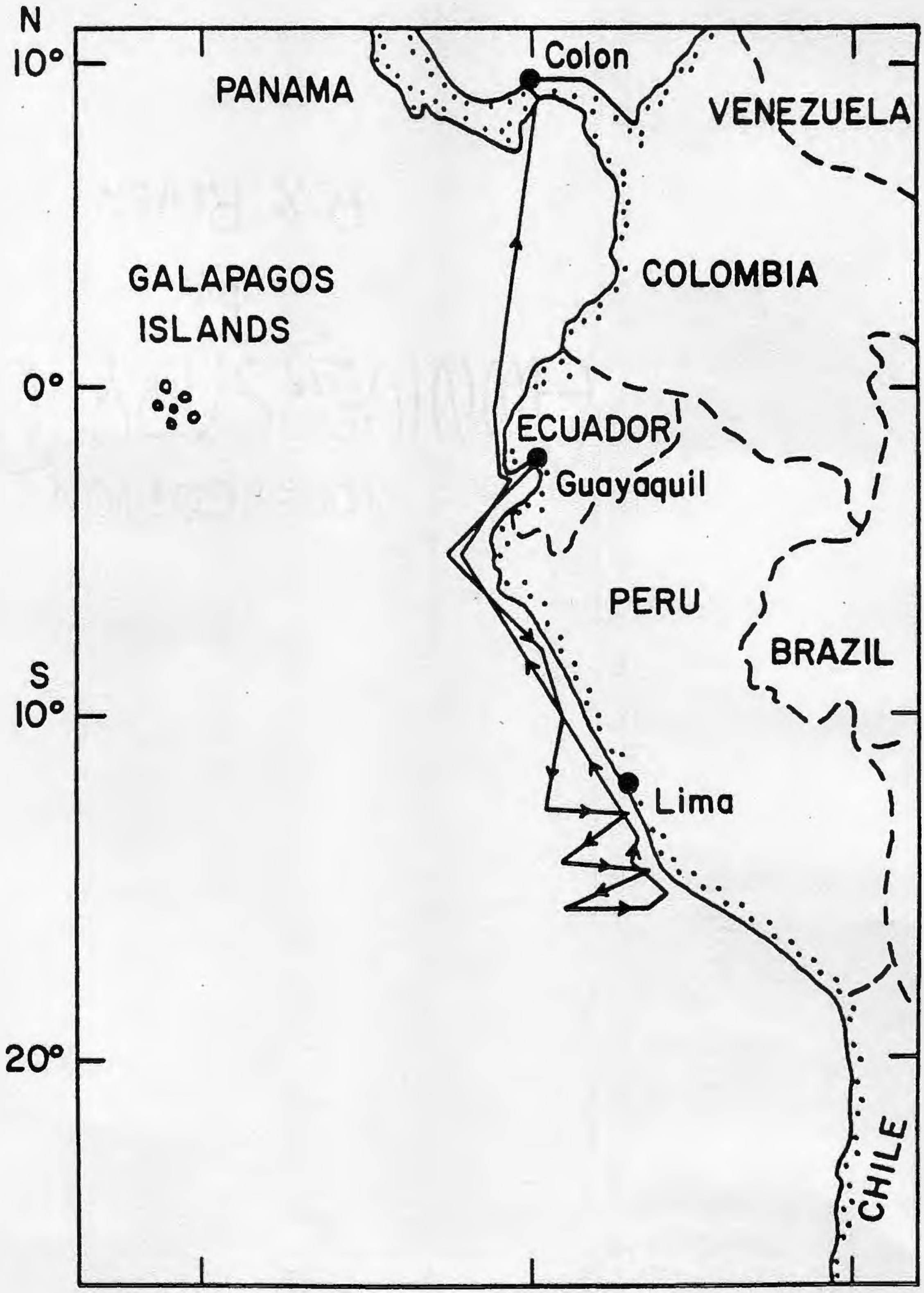
In addition to the filter samples, surface microlayer and subsurface water samples were taken at the sampling site, both at the beginning and end of the sampling runs. The microlayer sampling used the screen technique of Garrett (1965). Reactive phosphorus was determined on the samples immediately on return to the laboratory. Samples for total phosphorus were transferred to brown glass containers and stored with Hg_2Cl_2 preservative until analysis. Samples for sodium analysis were stored in polyethylene bottles.

AEROSOL SAMPLING

Samples of atmospheric particulate matter were collected on R/V TRIDENT Cruise 165 in the Peru current near the coasts of Ecuador and Peru. This area is high in surface water phosphorus because of the coastal upwelling; thus it appeared to be an ideal location in which to look for evidence of phosphorus injection into the atmosphere. Figure 3 shows the cruise track of TR-165.

Filter samples were taken on the TRIDENT using an atmospheric sampling tower mounted on the bow of the ship. Filter holders mounted on this tower are about 15 m above the ocean surface and are slightly forward of the bow. The filter holders have been found to be well in front of any bow spray. Phosphate samples were collected on 20 x 25 cm Delbag Microsorban 97/99 filters using high-volume air sampling pumps. To eliminate contam-

Fig 3. Cruise track of R/V TRIDENT Cruise 165


N
10°
PANAMA
Colon
VENEZUELA
COLOMBIA
GALAPAGOS
ISLANDS
0°
ECUADOR
Guayaquil
PERU
BRAZIL
S
10°
Lima
20°
CHILE
90°W
80°
70°

ination from the pumps, they were located on the deck well behind the tower and connected to the filter holders by flexible tubing. To prevent contamination of the sample by emissions from the ship, a Directional Air Sampling Control System was used. Sampling only occurred when the wind was ± 60° off the bow. Sampling times ranged from 24 to 48 hours, and air sampling volumes were between 1300 m^3 and 3300 m^3, STP.

ANALYSIS OF SAMPLES

Sodium was determined on the BIMS filter samples and water samples by neutron activation analysis. Sodium, aluminum, and vanadium were determined by neutron activation on the TRIDENT cruise samples. One quarter of the filter was pelletized and irradiated for 30 s in the Rhode Island Nuclear Science Center swimming-pool reactor at a flux of 4×10^{12} $n\ cm^{-2}s^{-1}$. Within two minutes the samples were counted for 400 s on a Ge(Li) detector (38cc volume, 7% efficiency, resolution 2.3 KeV for the 1332 KeV gamma ray of ^{60}Co) coupled to a Nuclear Data 2200 4096 channel analyzer with a computer compatible magnetic tape output (Ampex TM-7) for spectrum analysis. A computer program (J.L. Fasching, personal communication) was used to process the Ge(Li) spectra acquired. Absolute standards for each element were prepared on blank filters, pelleted, irradiated and counted in the same manner as the unknowns. Constant geometry was maintained during the counting of all standards and unknowns. Corrections were made for dead time and half-life discrimination.

Water samples were analyzed for sodium by spotting a known amount of sea water on a 2.2 cm W-41 disk which was then sealed in polyethylene. The samples were irradiated for between 2 and 4 hours and counted two days later on a Ge(Li) detector (60cc volume, 11% efficiency, resolution of 2.5 KeV for the 1332 KeV gamma ray of ^{60}Co) coupled to a Northern 8192, 4000 channel analyzer operating with a DEC PDP-11 computer. These water sodium values are those of S.R. Piotrowicz (1977) and are used with his kind permission.

After decay of any residual activity, the pelletized filters were ashed at 550°C in the presence of excess magnesium. The residue was dissolved in 1 ml of 1 N HCl, diluted to 40 ml and filtered. Phosphorus was determined by the ascorbic acid method of Murphy and Riley (1962). Phosphorus determined in this manner is called "total phosphorus".

For all the cruise samples, and for two of the BIMS samples where the filters were avilable, an additional quarter of the filter was extracted for 30 minutes in doubly distilled water. After filtration, phosphorus was determined colorimetrically as above. This phosphorus fraction is called "reactive" phosphorus.

"Total" phosphorus on the filtered water samples was determined using the persulfate oxidation method of Menzel and Corwin (1965) followed by the ascorbic acid method of Murphy and Riley (1962). "Reactive" phosphorus was determined on filtered water samples by the same method as the filter samples.

"Organic" phosphorus was caluclated as the difference between "total" phosphorus and "reactive" phosphorus.

The overall sample variations including analytical precisions are estimated to be: phosphorus on the filter samples, ± 10%; phosphorus in the water samples, ± 4%; sodium, ± 5%; aluminum, ± 6%; vanadium, ± 11%.

RESULTS

Definition of Enrichments

The discussion on the BIMS field study which follows will use the term "enrichment" (E) frequently. Following the recommendations of the Working Symposium on Sea-to-Air Chemistry (Duce et al., 1972) enrichment is defined as:

$$E = \frac{(P/Na)_{aerosol}}{(P/Na)_{water}} - 1 \qquad (1)$$

A value of zero, then, represents no enrichment.

Whenever enrichments in the sea surface microlayer compared to the underlying water are considered, the sodium concentrations in the microalyer and subsurface water samples are assumed to be equal. Equation 1 then reduces to

$$E = \frac{P_{microlayer}}{P_{subsurface}} - 1 \qquad (2)$$

Results of the BIMS Study

The amounts of both phosphorus and sodium that are collected on the filters appear to depend upon wind velocity (Figure 4) and bubbling depth (Figure 5) with less material being collected under conditions of high winds or deep bubbling. The wind velocity given is a subjective estimate of the velocity at the time of collection of the sample on a 1-10 scale. No wind is indicated by 1, while 10 is the maximum wind velocity in which the BIMS could be operated (7-8 m s^{-1}). The decrease in material collected with increasing wind velocity most likely reflects the difficulty in keeping the cone of the BIMS over the bursting bubbles under conditions of high winds and rough seas. The decrease in material collected as the bubbling depth increases may also be due to failure to capture all the droplets from the bursting bubbles. The cone is more

Fig. 4 Effect of wind velocity on the absolute amounts of phosphorus and sodium collected on BIMS filters

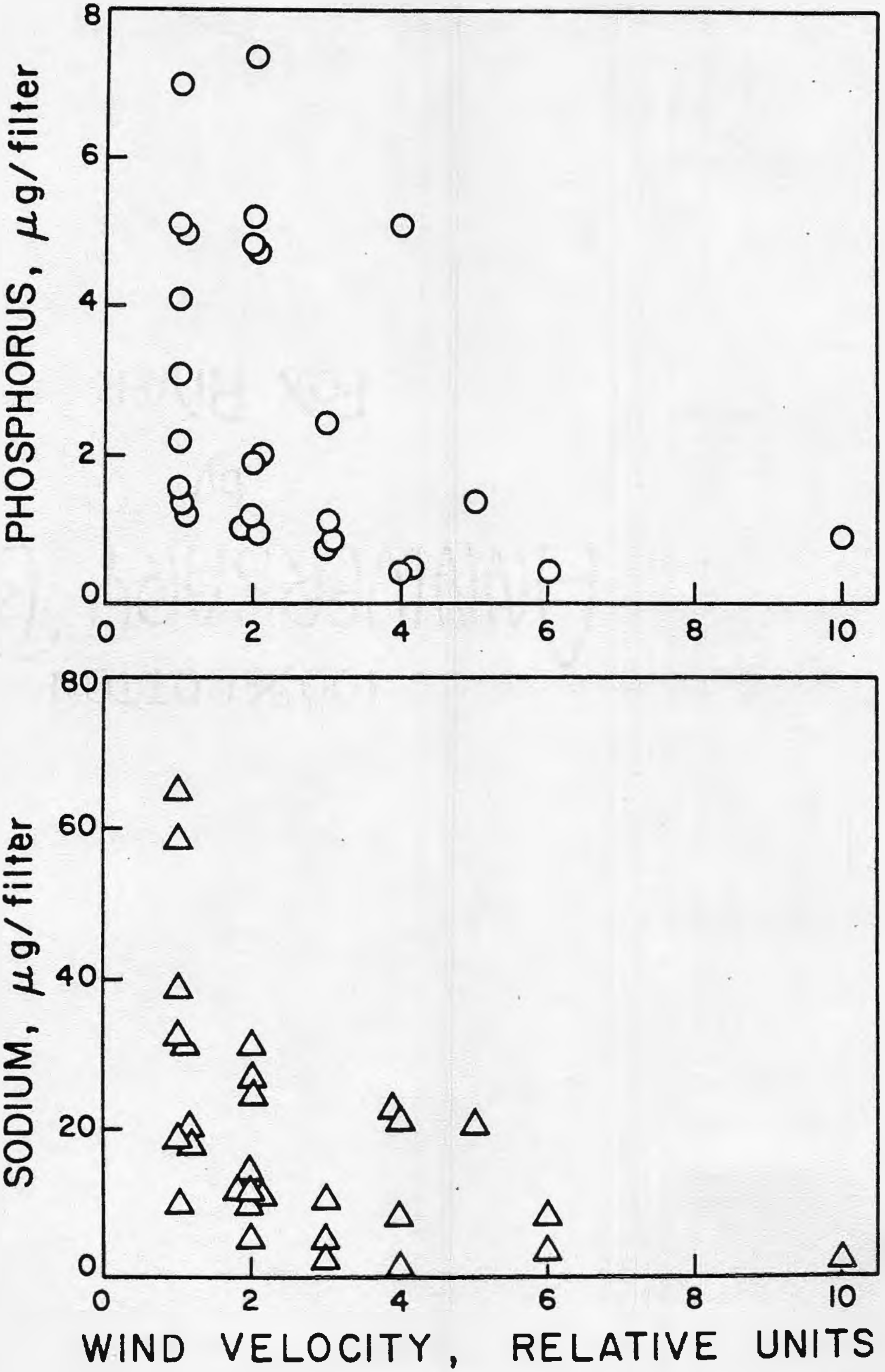
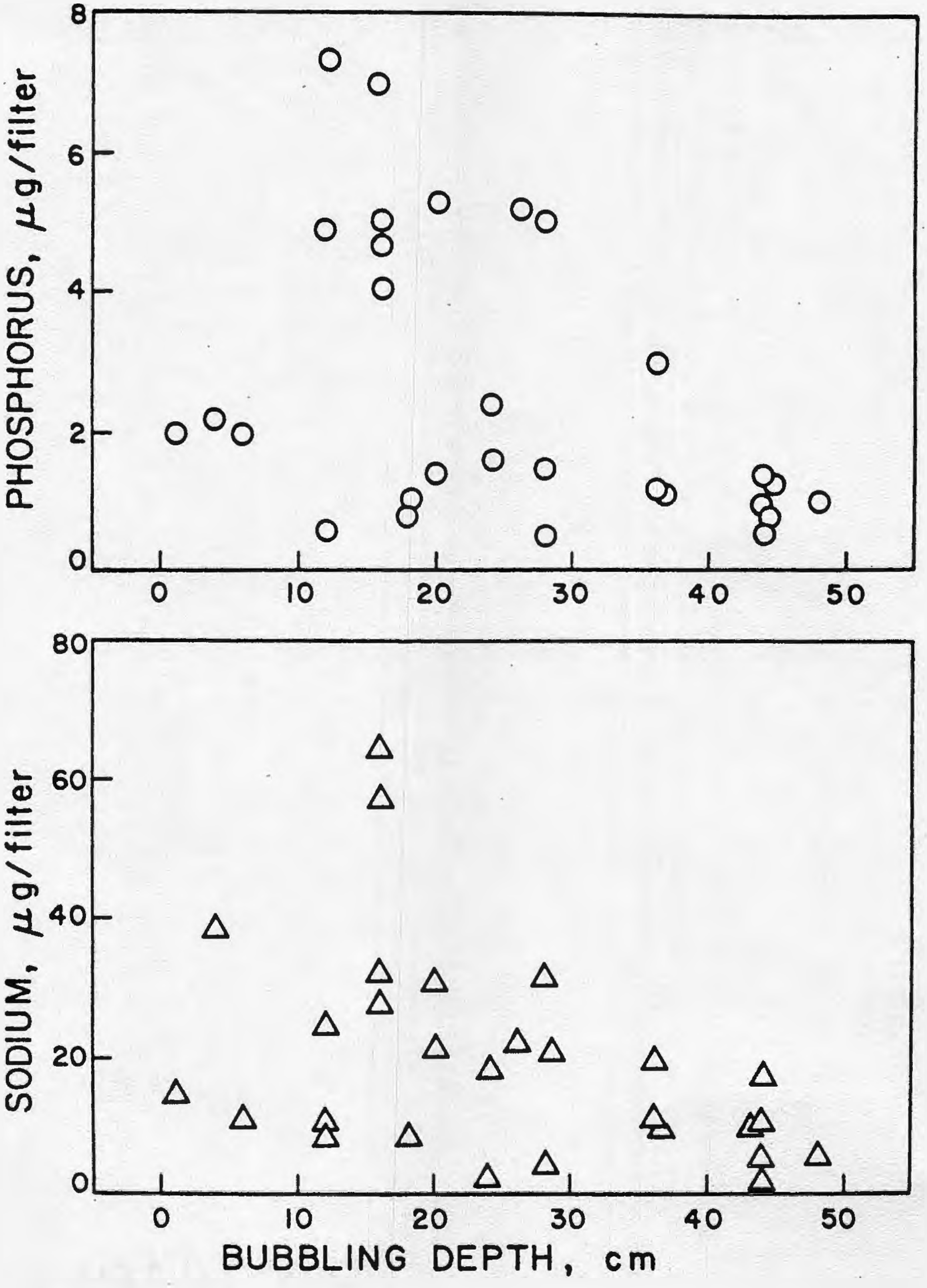

PHOSPHORUS, μg/filter
0
2
4
6
8
SODIUM, μg/filter
0
20
40
60
80
0
2
4
6
8
10
WIND VELOCITY, RELATIVE UNITS

Fig. 5 Effect of bubbling depth on the absolute amounts of phosphorus and sodium collected on BIMS filters


PHOSPHORUS, μg/filter
0
2
4
6
8
0
10
20
30
40
50
SODIUM, μg/filter
0
20
40
60
80
0
10
20
30
40
50
BUBBLING DEPTH, cm

difficult to hold over bursting bubbles which are generated at depth than over those generated just under the water surface. However, bubbles generated at 40-50 cm may also coalesce before reaching the surface. Thus fewer drops may be ejected from the water surface during deep bubbling.

The phosphorus enrichments found on each BIMS sample are given in Table I and shown as a function of bubbling depth in Figure 6 and of subsurface phosphorus concentration in Figure 7. Figure 6 shows that there is no consistent pattern to the observed enrichments as a function of bubbling depth. From these data, I infer that the correlation between the amounts of phosphorus and sodium found on the filters with bubbling depth represent a decrease in the number of drops reaching the filter rather than a change in concentration of these elements in the drops. In addition, the independence of enrichment and bubbling depth suggests that the source of this phosphorus is the sea surface microlayer rather than the subsurface water.

If significant bubble scavenging of P from subsurface water were occurring, one would expect to find enrichments increasing as bubbling depth increases. This effect has been found to occur for Zn (Piotrowicz, 1977). Figure 7 also suggests that the microlayer is the source of the phosphorus. Enrichment is seen to be inversely correlated with the subsurface phosphorus concentration. This same correlation was found in the laboratory study of MacIntyre (1965). This inverse correlation would be expected to occur if the concentration of phosphorus at the microlayer were reasonably constant and, within the range of phosphorus concentration found in Narragansett Bay, independent of the subsurface concentration. Concentration of organic-phosphorus compounds at the sea surface is one way that this might occur.

TABLE I

RESULTS OF BIMS BUBBLING EXPERIMENTS IN NARRAGANSETT BAY

DAY SAMPLED 1975	WATER SAMPLES		FILTER SAMPLES			
	TOTAL P µg/l	SODIUM mg/l	BUBBLING DEPTH cm	TOTAL P µg	SODIUM mg	ENRICHMENT $E_{(Na)}$
May 9	45.3	9930	24	2.4	2.7	170
			44	0.53	2.0	51
May 29	53.0	9600	2	2.0	14.8	23
			26	5.2	22.6	41
			48	1.0	5.7	32
June 27	92.8	9360	6	1.9	11.8	16
			12	0.58	3.6	6
			18	0.76	8.3	8
			18	0.97	3.0	31
July 16	75.7	7900	23	0.46	3.7	12
			36	1.1	10.4	10
			44	0.84	5.3	15
July 23	92.4	9940	20	1.4	21.3	6
			28	1.5	21.6	6
			44	1.0	11.9	8
July 30	95.8	9220	12	4.8	11.4	39
			12	7.4	24.3	29
			16	4.7	27.0	16
			20	5.2	31.2	15
			28	5.0	31.3	14
			36	3.1	20.0	14
			44	1.3	10.0	11
August 13	107	9260	4	2.2	28.5	4
			16	4.1	32.3	10
			16	5.1	64.8	6
			24	1.6	18.4	10
			36	1.2	11.6	8
			44	1.4	17.2	6

Fig. 6 Phosphorus enrichment as a function of bubbling depth. Aerosol samples collected on the same day have the same symbol.

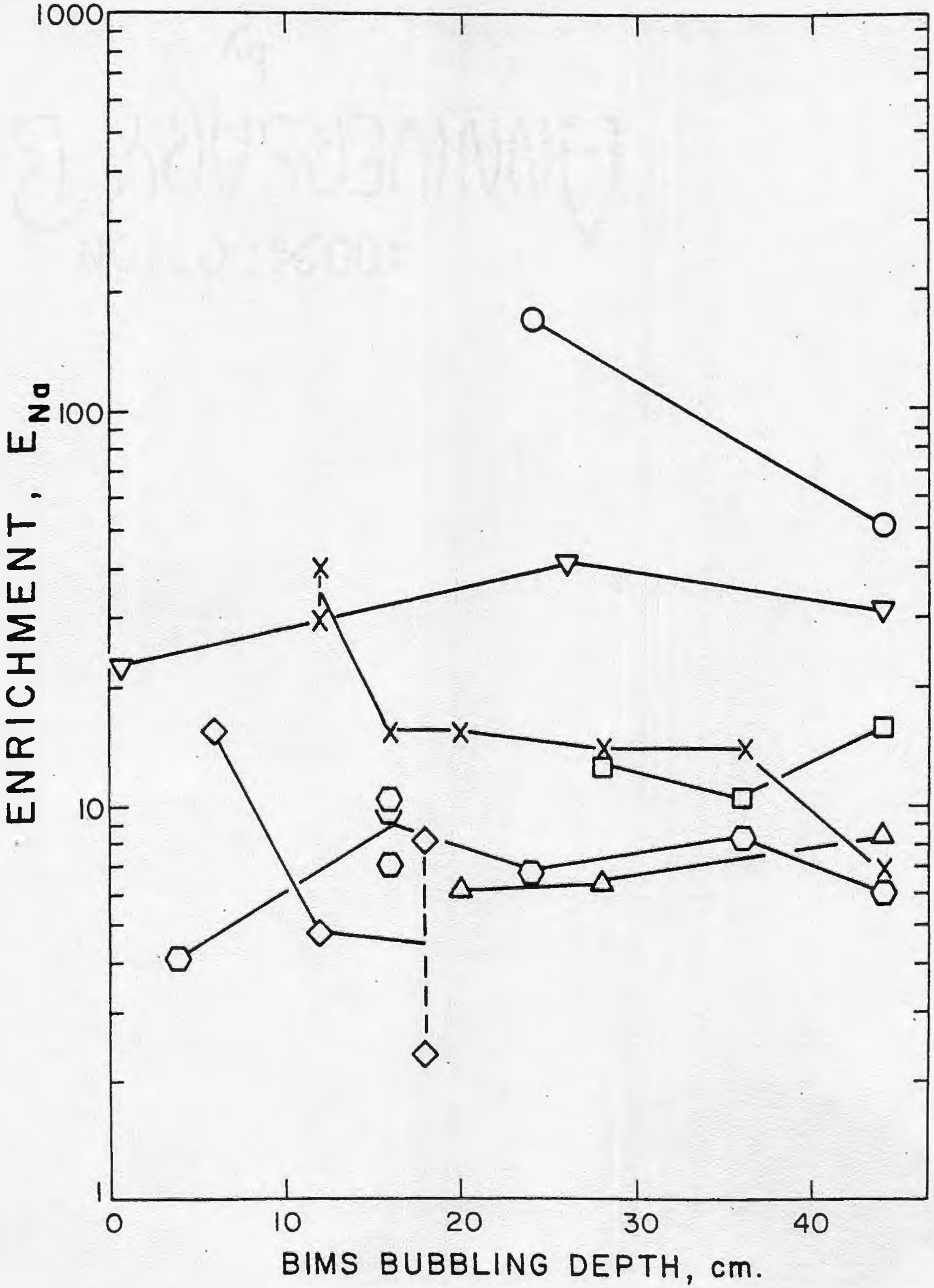

1000
100
10
1
ENRICHMENT, E_{Na}
0
10
20
30
40
BIMS BUBBLING DEPTH, cm.

Fig. 7 Phosphorus enrichment as a function of phosphorus concentration in the subsurface water.

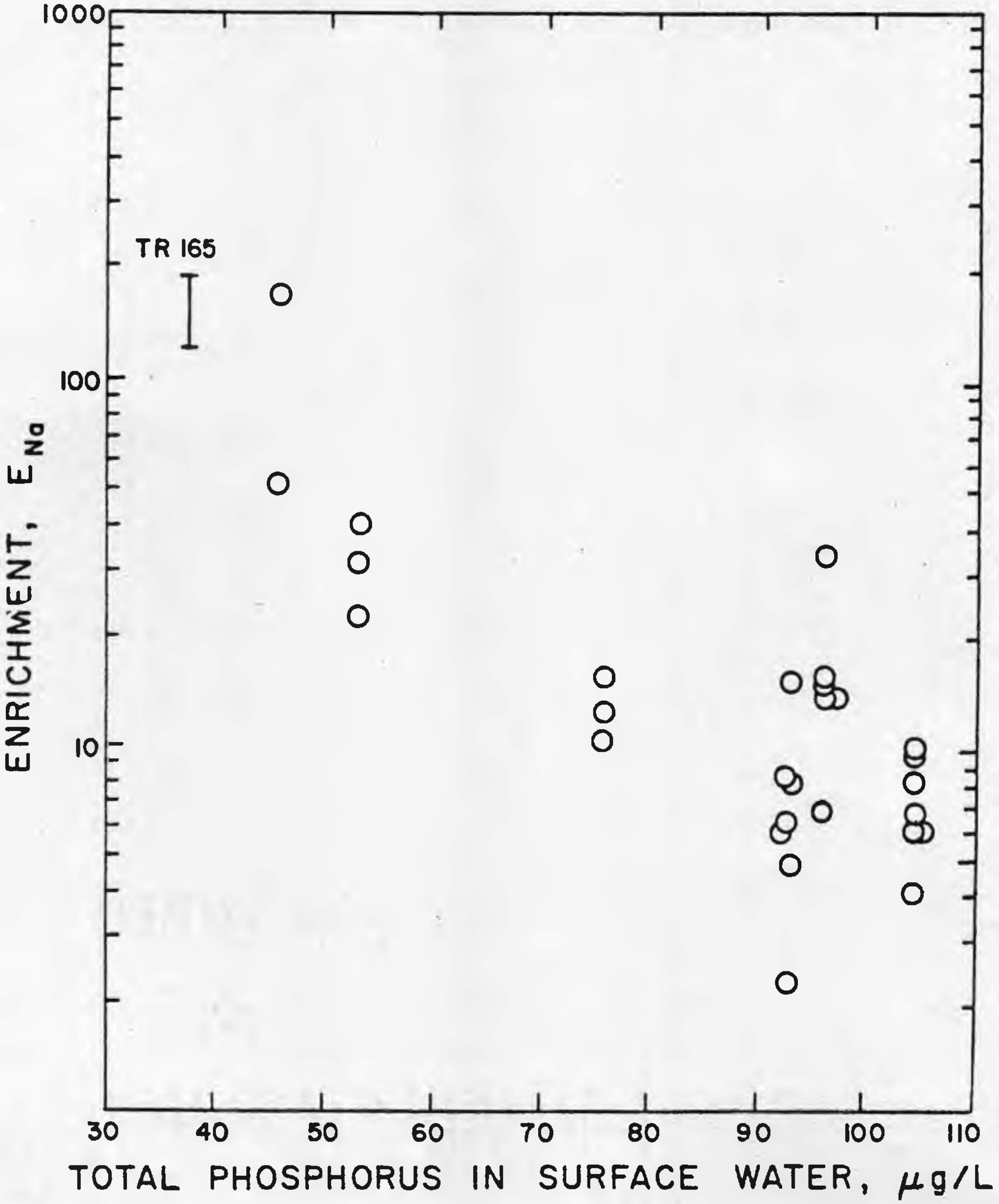

1000
100
10
ENRICHMENT, E_{Na}
TR 165
30
40
50
60
70
80
90
100
110
TOTAL PHOSPHORUS IN SURFACE WATER, μg/L

Figure 8 shows enrichment of total phosphorus as a function of wind velocity for all BIMS samples collected over water with total phosphorus concentration between 92 and 96 μg l^{-1}. The two upper points at wind velocity 2 represent samples taken while bubbling in a visible surface slick. The other samples were all collected over water which had no visible surface slick. The enrichments found on the non-slick samples appear to decrease between wind states 1 and 6. This decrease would also be consistent with the microlayer being the main source of phosphorus on these samples. Disruption of the microlayer with increasing wind velocity should reduce the amount of material at the surface available for ejection.

Similar behavior has been found in the organic phosphorus portion of the sea surface microlayer. Unpublished data of phosphorus enrichment in the microlayer obtained by M.E.Q. Pilson and D.R. Kester have been plotted against the wind velocity at the time of sampling. Organic phosphorus enrichment is plotted against wind velocity in Figure 9, reactive phosphorus enrichment against wind velocity in Figure 10. The enrichment of organic phosphorus in the microlayer is seen to decrease with increasing wind velocity. The major decrease in enrichment occurs between 0.5 and 2 m s^{-1} wind velocity. The surface-active organic phosphorus compounds present in sea water should be soluble surfactants. The behavior of soluble surfactants in a monolayer at the water surface is complex, unlike insoluble surfactants, the soluble surfactants are capable of diffusing into the form the bulk water as a function of wind stress and wave action (Davies and Rideal, 1961). While the exact mechanism is not clear, it appears that, as wind stress increases, increasing amounts of organic phosphorus are driven from the microlayer into the subsurface waters. Reactive-phosphorus enrichment, on the other

Fig. 8 Enrichment as a function of wind velocity

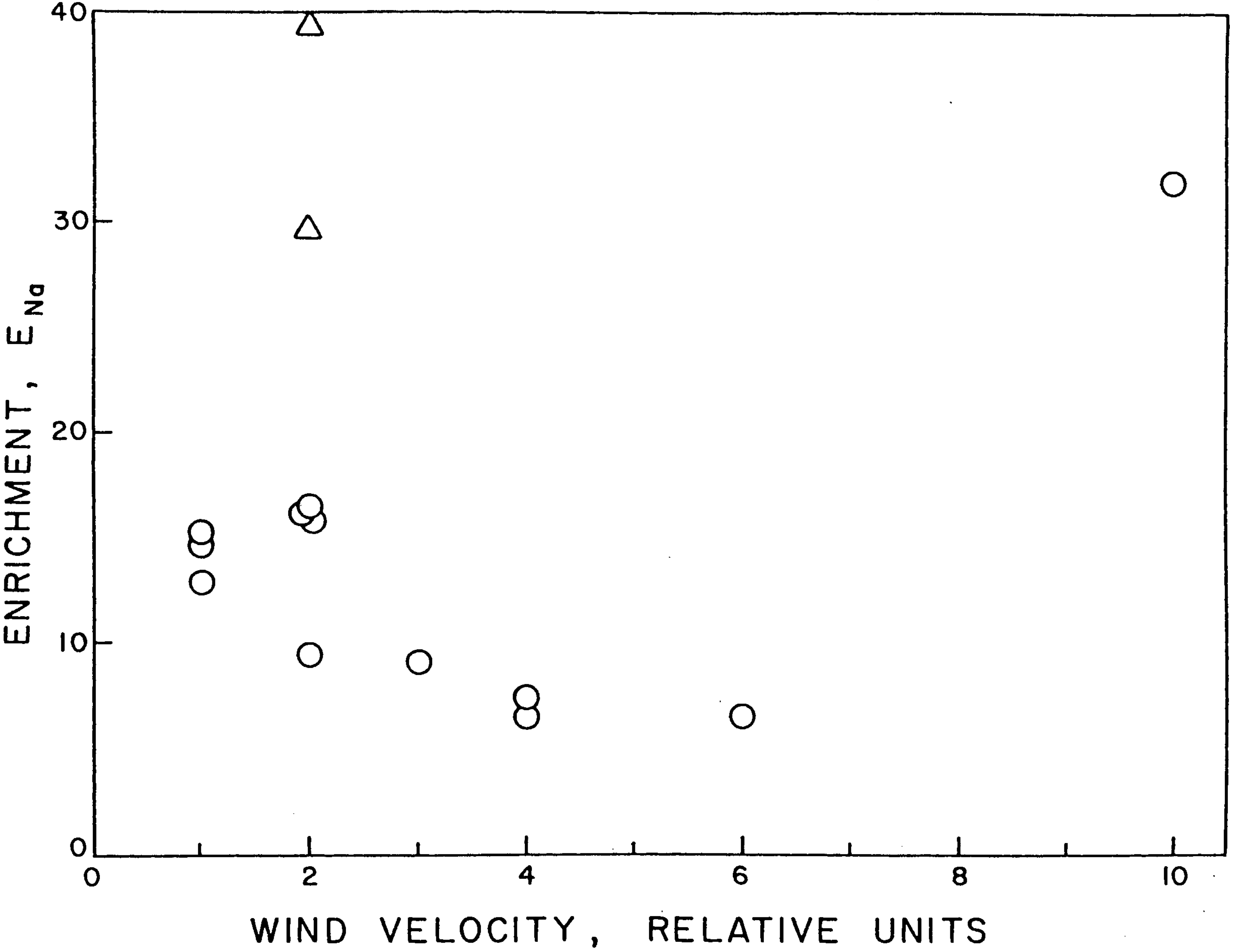

ENRICHMENT, E_{Na}
0
10
20
30
40
0
2
4
6
8
10
WIND VELOCITY, RELATIVE UNITS

Fig. 9 Enrichment of organic phosphorus in the microlayer as a function of wind velocity.

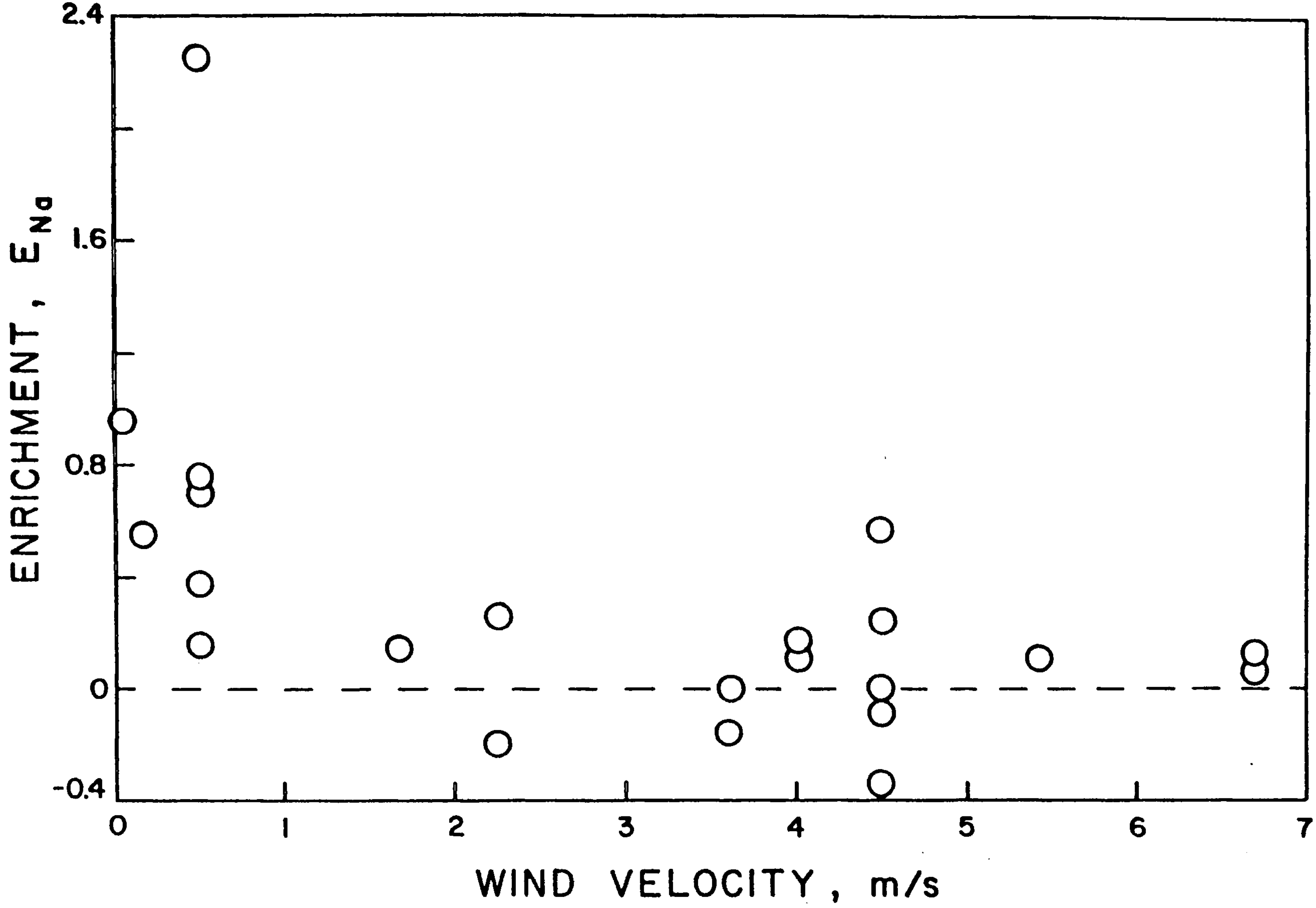
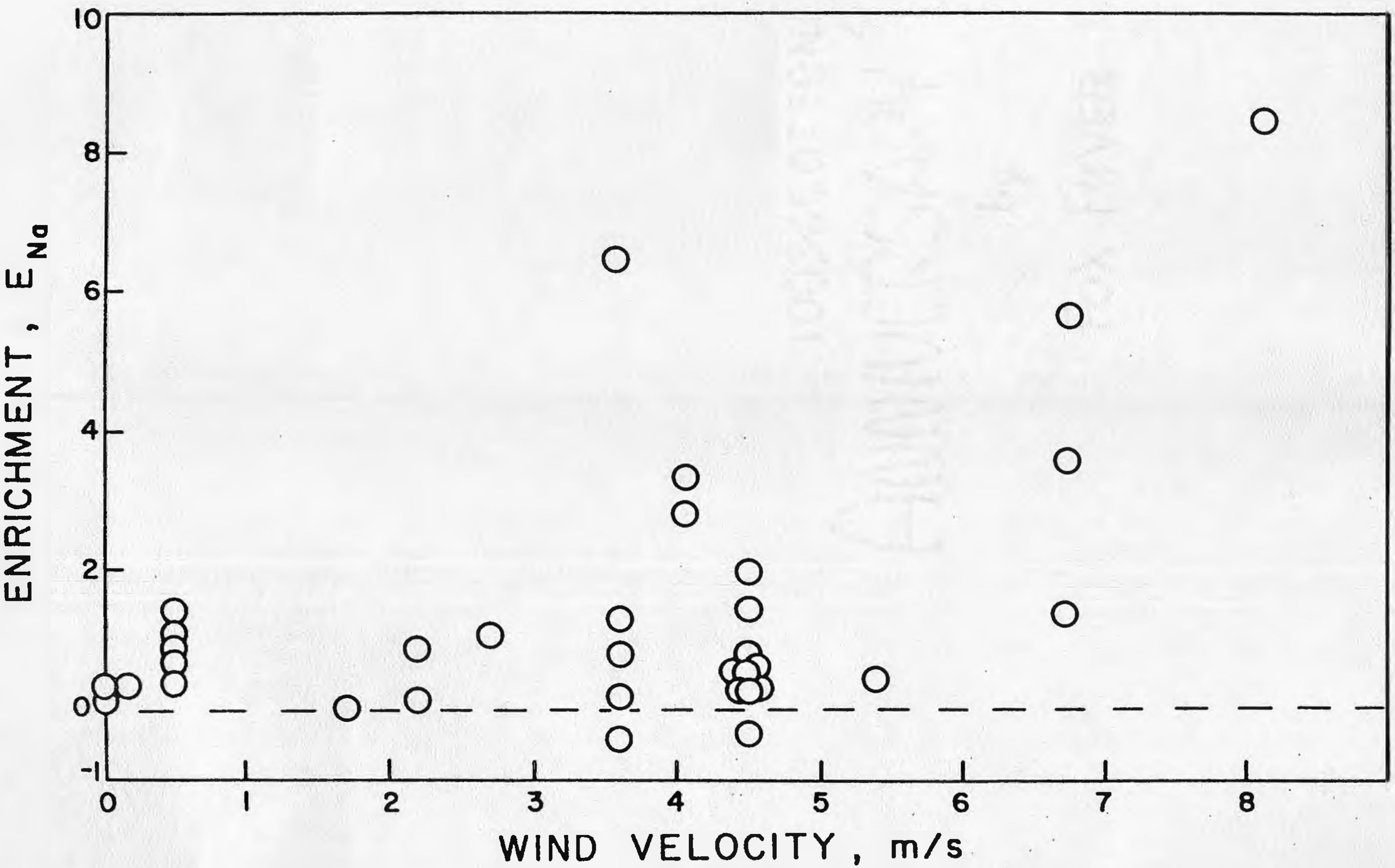

ENRICHMENT , E_{Na}
2.4
1.6
0.8
0
-0.4
0
1
2
3
4
5
6
7
WIND VELOCITY , m/s

Fig. 10 Enrichment of reactive phosphorus in the microlayer as a function of wind velocity.


ENRICHMENT , E_{Na}
10
8
6
4
2
0
-1
0
1
2
3
4
5
6
7
8
WIND VELOCITY , m/s

hand, appears to be proportional to wind stress, increasing with the square of the wind velocity (Figure 10). The number of bubbles bursting at the sea surface would also be expected to be proportional to wind stress. The behavior of reactive phosphorus with wind stress is explicable if reactive phosphorus is scavenged by bubbles which are injected into the surface waters. Some of this phosphorus is then deposited in the microlayer when the bubbles burst at the water surface. With this mechanism, high wind stress should lead to greater transport of phosphorus to the microlayer, reduced phosphorus in the subsurface waters, and thus higher enrichments. The high enrichment at the wind velocity of 10 shown in Figure 8 may due be due to this hypothetical mechanism.

Both BIMS aerosol and water samples from the runs of July 30 and August 13 were analyzed for the "organic" and "reactive" fractions of phosphorus. The results are presented in Table II. Organic phosphorus is seen to be enriched about one order of magnitude more than reactive phosphorus in the aerosol samples. The difference in enrichments between the organic and reactive phosphorus fractions in the filter samples is much greater than that observed in the microlayer samples. This suggests that the true microlayer is much thinner than the 300-400 μm that is the reported sampling depth of the screen sampler (Hatcher and Parker, 1974).

Enrichment values for organic phosphorus of 40-180 are the same order of magnitude as the enrichments of Fe, Cu and Zn measured by Piotrowicz (1977) and may support the hypothesis that organic associations are important in controlling the enrichment of these elements (Piotrowicz, 1977).

Reactive phosphorus enrichments are between 3-8, in good agreement

TABLE II

MICROLAYER AND BIMS AEROSOL ENRICHMENTS OF REACTIVE AND ORGANIC PHOSPHORUS FRACTIONS

SAMPLE	DATE OF SAMPLING			
	July 30, 1975		August 13, 1975	
Water Samples				
Reactive P				
Microlayer conc-μg/l	52.7		36.4	
Subsurface conc-μg/l	51.6		28.6	
Enrichment	0.02		0.27	
Organic P				
Microlayer conc-μg/l	27.8		31.6	
Subsurface conc-μg/l	23.5		23.0	
Enrichment	0.18		0.37	
Sodium conc mg/l	9220		9260	
Aerosol Samples	1	2	1	2
Reactive P - μg	1.4	0.37	0.47	0.57
Organic P - μg	10.7	7.8	4.5	3.4
Sodium - mg	36.5	17.1	39.0	34.5
Reactive P - $E_{(Na)}$	6	8	3	4
Organic P - $E_{(Na)}$	114	177	46	38
Total P - $E_{(Na)}$	40	62	22	19

with those measured in the laboratory by MacIntyre (1965, 1968). The much lower enrichments measured for the reactive phosphorus fraction indicate a much reduced propensity to concentrate at the microlayer or to adsorb onto bubbles. From this study, I conclude that the greater part of any phosphorus injected into the atmosphere by bubble action in the oceans should be organic.

Evidence for phosphorus injection from the oceans

The area of the Peru current near the coasts of Peru and Ecuador was chosen as the test area to determine if oceanic phosphorus can be found in the marine atmosphere. Due to the intense upwelling that occurs near the coast, phosphorus concentrations are high in the surface waters. The concentration of total phosphorus was determined on filtered surface water from 11 stations in the current. Total phosphorus ranged from 0.6 to 2.5 $\mu M\ l^{-1}$, with a mean of 1.2 $\mu M\ l^{-1}$. Wind velocities during sampling were between 3.6 and 9.4 $m\ s^{-1}$, and averaged 7.1 $m\ s^{-1}$. Whitecaps and breaking waves were present on the ocean surface at all times.

As the atmospheric particulate filter samples were collected between 10 and 2000 km from the coast, the filters contain significant amounts of continental material along with the sea salt. Because the phosphorus on the filters has no obvious tag indicating its source, it is necessary to correlate the phosphorus by statistical techniques to tracers which are assumed to represent a specific source region or material. Aluminum is a major component of the crustal aerosol and is taken in this study as an indicator of continental material. Sodium, after correction for the contribution of crustal material using the Na/Al ratio from Mason

(1966) is taken as the sea salt tracer. Excess vanadium, that present over the amount expected based on crustal V/Al ratios (Mason, 1966) is used as a tracer for anthropogenic sources. Excess vanadium is an excellent indicator of particulate input from certain combustion processes (Duce and Hoffman, 1976). Table III gives the concentrations of the phosphorus fraction and tracer elements along with the midpoint locations of the samples.

The statistical methods applied to the data are those of factor analysis and multivariate linear regression. Factor analysis is a statistical technique for the grouping of linear combinations of similar variances from variables that are highly correlated. The theory of factor analysis has been presented in detail by Harman (1967). The results of the factor analysis of the filter samples are presented in Table IV. The three factors presented sum to 97% of the total variation. The first factor shows a strong association between sea salt sodium and organic phosphorus. Some aluminum variation also appears to be associated with this factor, which appears to represent a marine source. Factor 2 contains most of the variation in excess vanadium and is surely the anthropogenic input from local combustion sources, including shipping in the area. Some reactive and organic phosphorus variation is associated with this factor. Soot particles from the combustion of diesel fuels and coal contain phosphorus (Smith, 1962; Linton et al. 1976). The exact chemical form of this phosphorus is not known, but it is not surprising that it should be water or acid soluble and thus show up in the phosphorus fractions called "reactive" and "organic". The third factor is clearly one representing a crustal source. The greater part of the aluminum and the reactive phosphorus variations are associated with this source.

I examine the data also using multivariate linear regression equations.

TABLE III

SAMPLE LOCATIONS AND ELEMENTAL CONCENTRATIONS OF TR 165 ATMOSPHERIC PARTICULATE SAMPLES

	MIDPOINT LOCATION		MEAN WIND	PHOSPHORUS		SODIUM	ALUMINUM	VANADIUM
SAMPLE	LATITUDE	LONGITUDE	ms^{-1}	REACTIVE ng m^{-3}	ORGANIC ng m^{-3}	μg m^{-3}	ng m^{-3}	ng m^{-3}
1	5°15'S	81°00'W	8.3	5.0	6.7	10	350	2.3
2	8°45'S	79°40'W	8.2	4.8	4.6	5.6	290	2.2
3	10°43'S	79°06'W	8.0	5.2	2.7	5.8	420	1.4
4	13°13'S	77°48'W	8.6	6.2	2.7	4.1	260	2.1
5	13°58'S	77°33'W	8.6	3.3	2.3	3.6	200	1.7
6	14°55'S	77°10'W	6.7	4.0	1.9	2.9	250	2.2
7	15°05'S	77°10'W	6.2	4.0	1.4	–	–	–
8	15°13'S	77°10'W	9.4	2.5	0.7	2.7	90	0.6
9	14°03'S	76°07'W	6.0	4.5	1.7	3.2	250	2.3
10	10°02'S	78°54'W	4.6	2.3	3.0	4.1	130	1.5
11	5°28'S	80°57'W	3.6	3.4	3.0	4.5	220	2.9

TABLE IV

FACTOR ANALYSIS OF TR 165 ATMOSPHERIC PARTICULATE SAMPLES

	FACTOR 1 MARINE	FACTOR 2 ANTHROPOGENIC	FACTOR 3 CRUSTAL
Eigenvalues	3.06	0.94	0.84
Portion	0.61	0.19	0.17
Cum. Portion	0.61	0.80	0.97
VARIANCE			
Reactive P	0.146	-0.240	0.930
Organic P	0.889	-0.374	0.236
Sodium	0.951	0.024	0.282
Aluminum	0.425	0.003	0.862
Excess Vanadium	0.132	-0.978	0.137

The total phosphorus, organic phosphorus, and reactive phosphorus concentrations were individually regressed against the sodium, aluminum, and vanadium tracers. The results of regression analyses of reactive, organic, and total phosphorus are given in Table V. Of particular interest here is an examination of the coefficients of the individual independent tracer element variables. These coefficients are ratios of the phosphorus from a given source to the tracer element representing that source. These ratios can be interpreted by comparing them with other experimental and published data.

The ratio of phosphorus to aluminum is 0.010 ± 0.002 in the total-P regression and 0.011 ± 0.003 in the reactive-P regression. These two values are not significantly different. These ratios are very close to crustal ratio of P/Al which is 0.013 (Mason, 1966). It appears, then, that the reactive phosphorus source is likely to be crustal material from the coastal deserts of Peru and Chile. Fig. 11 shows the dependence of reactive phosphorus on aluminum.

Total phosphorus is also significantly correlated with excess vanadium with a coefficient of 1.87 ± 0.55. A phosphorus-to-vanadium ratio of 1.6 can be calculated for coal flyash using the data of Linton et al. (1976), while a value of 0.2 is obtained from the analysis of fuel-oil soot particles reported by Smith (1962). Thus there is evidence for an input of anthropogenic phosphorus from combustion sources, and a portion of the phosphorus in these aerosol samples appears to be from this source.

The most important ratios from the standpoint of this study are the coefficients found for the sea salt sodium term. Fig. 12 illustrates this dependence for organic phosphorus. The ratios are 0.63 ± 0.09 for the

TABLE V

RESULTS OF MULTIVARIATE REGRESSION ANALYSIS OF TR 165 ATMOSPHERIC PARTICULATE SAMPLES

PHOSPHORUS FRACTION	REFERENCE ELEMENT	COEFFICIENT β	VARIATION OF COEFFICIENT	SIGNIFICANCE[1] Ho≠0	% VARIATION[2] EXPLAINED	TOTAL VARIATION[3] EXPLAINED
Reactive	Sodium	-0.090	± 0.168	0.39	24	70
	Aluminum	0.011	± 0.003	0.97	69	
	Excess Vanadium	0.583	± 0.587	0.64	7	
Organic	Sodium	0.631	± 0.088	0.99	84	95
	Aluminum	-0.0006	± 0.002	0.25	0	
	Excess Vanadium	1.27	± 0.307	0.99	16	
Total	Sodium	0.566	± 0.132	0.99	51	91
	Aluminum	0.010	± 0.002	0.98	34	
	Excess Vanadium	1.87	± 0.55	0.98	15	

[1] Probability that the coefficient is not equal to zero.

[2] The percentage of the total variation explained by the regression which is explained by a specific tracer.

[3] The percentage of the total sample variation explained by the regression.

Fig. 11 Reactive phosphorus as a function of aluminum in aerosol samples.

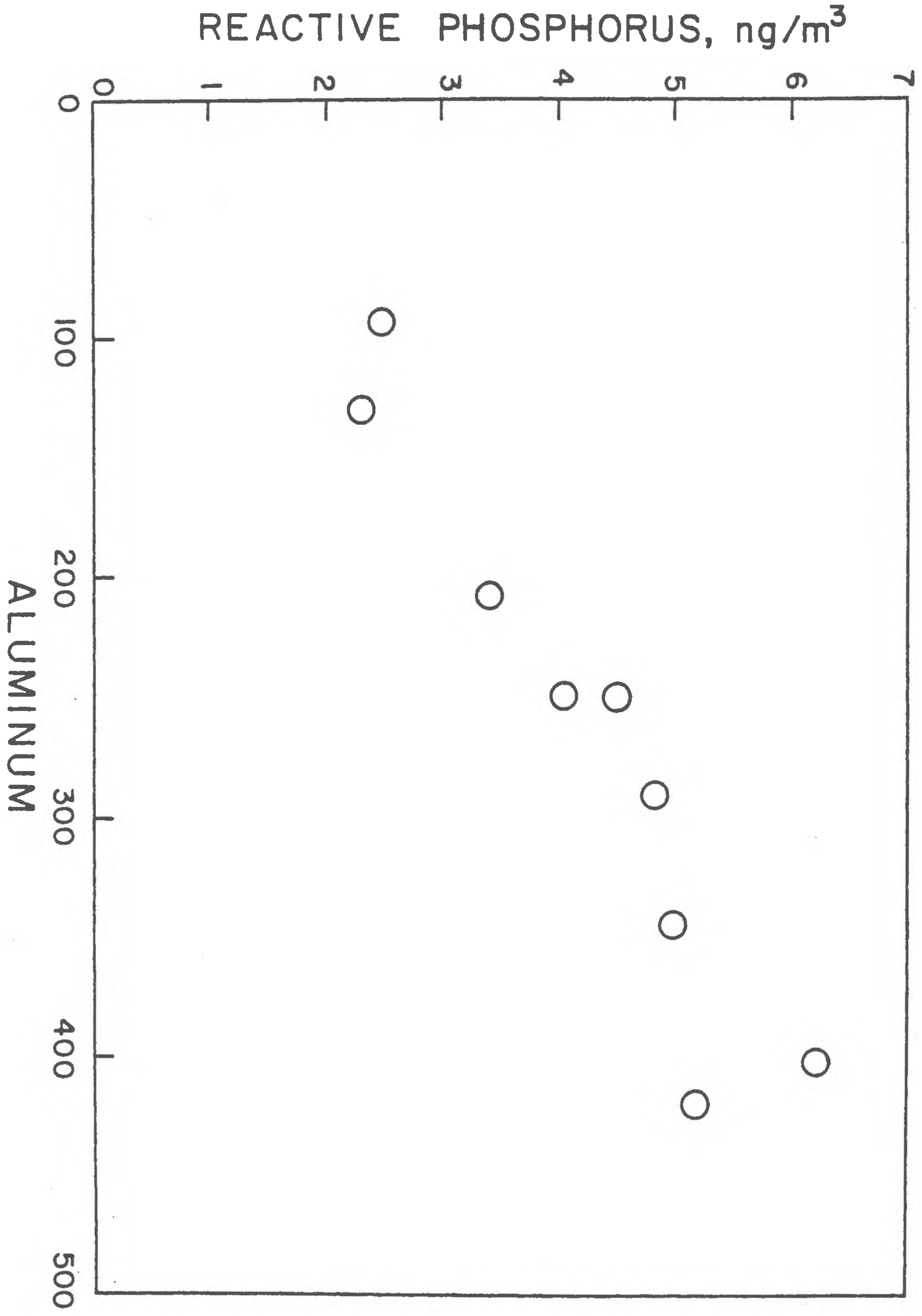
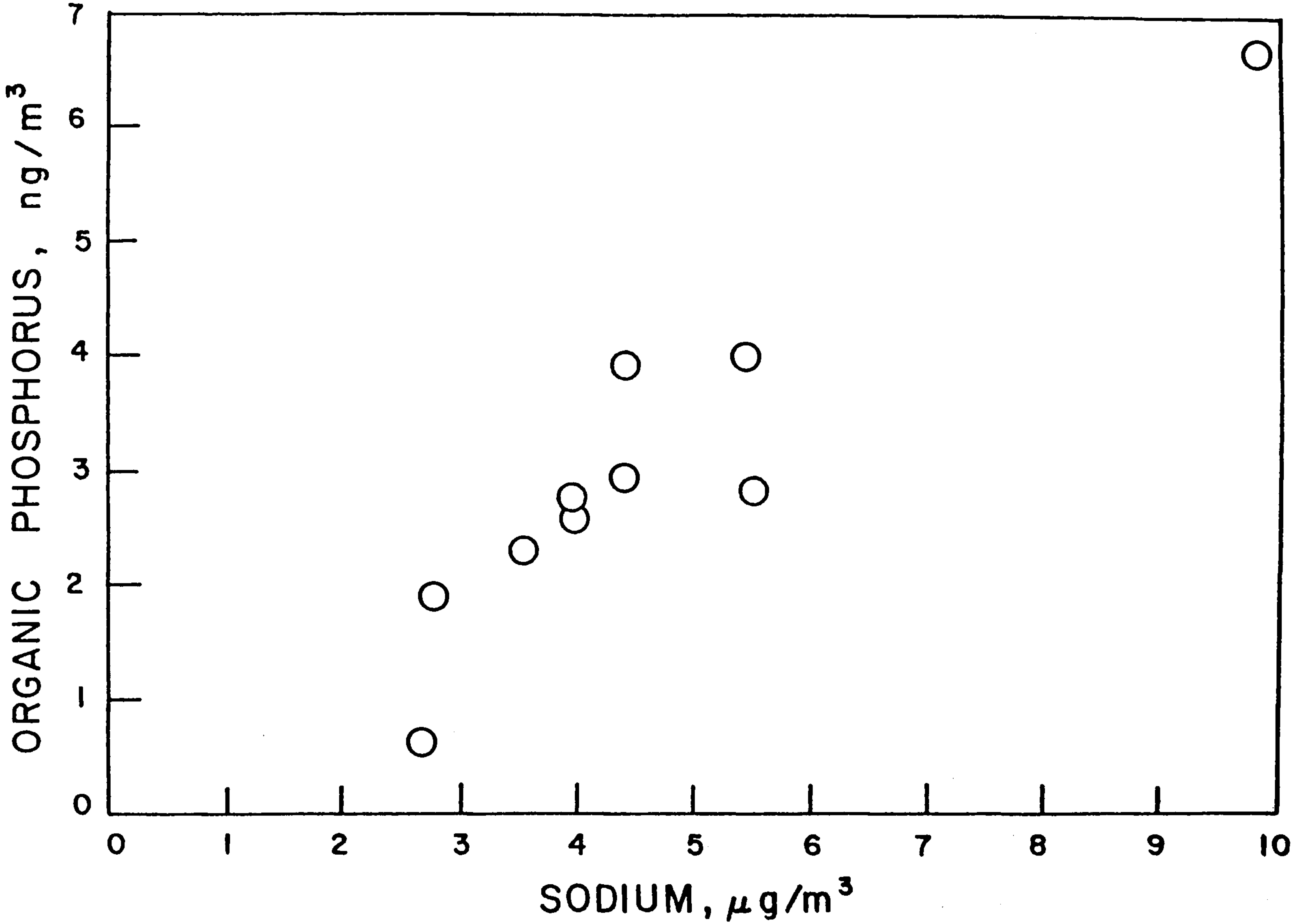

REACTIVE PHOSPHORUS, ng/m^3
0
1
2
3
4
5
6
7
ALUMINUM
0
100
200
300
400
500

Fig. 12 Organic phosphorus as a function of sodium in aerosol samples.


ORGANIC PHOSPHORUS, ng/m^3
0
1
2
3
4
5
6
7
0
1
2
3
4
5
6
7
8
9
10
SODIUM, µg/m^3

organic phosphorus regression and 0.57 ± 0.13 for the total phosphorus regression. These ratios are not statistically different. From these ratios and the mean phosphorus concentration of the surface waters of 37 ug l^{-1} I can estimate an enrichment factor for the marine phosphorus ejected from these waters. When I include the uncertainties from the statistical regressions in the calculation, I estimate the phosphorus enrichment to be between 125 and 220. This range is plotted in Figure 7 where it can be seen to be a not unreasonable extrapolation of the BIMS data.

I have shown that phosphorus from the ocean can be injected into the atmosphere. However, marine phosphorus is probably a significant nutrient source to terrestrial vegetation only if: (1) source waters relatively high in phosphorus are available; (2) winds are strong enough to cause significant bubble generation; and (3) winds are onshore a significant part of the time. For example, the prevailing winds off the west coast of South America are parallel to the coast and deliver little marine phosphorus to the land. In other locations conditions may be more favorable. It is possible that much of the phosphorus found in precipitation in Taita, New Zealand (Miller, 1961), in Nigeria and the Gambia during the wet season (Jones, 1961; Thorton, 1965) and on the Kerala Coast of India during the monsoon season (Vizayalokshni and Pandalai, 1963) comes from the adjacent oceans.

PARTICULATE PHOSPHORUS FORMATION

When the reports (Baylor et al., 1962; Sutcliffe et al., 1963) that suggest that dissolved phosphorus can be converted to particulate phosphorus by the action of bursting bubbles are reviewed in light of more recent knowledge of the chemistry and biology of sea water, some problem areas can be identified. The major one is the assumption that the sea water filtered through 0.45 μm filter was free of biological activity. Recent work (Sieburth, personal communication, 1977) shows that a significant portion of marine bacteria pass through a 0.45 μm filter. Bacteria themselves are enriched in the drops from bursting bubbles (Carlucci and Williams, 1965; Blanchard and Syzchek, 1970). It would appear that high concentrations of bacteria coupled with bubbling time of up to 24 hours (Baylor et al., 1962) could cause conversion of the reactive phosphorus by biological activity alone.

Intensive bubbling of sea water can cause flocs to form in the water, some of which are ejected in the drops from the bubbles (Sutcliffe et al., 1963). While most of the flocs are organic, inorganic floc formation has also been reported (MacIntyre, 1965). Bubbling rates in the experiments of Sutcliffe et al., (1963) and MacIntyre (1965) were much higher than those that occur naturally in the open ocean. Wallace (1976) calculated the steady state open ocean surface area input of bubbles to be 3.1 $cm^2 m^{-2} sec^{-1}$. Baylor et al. (1962) reports using 800 $cm^3 min^{-1}$ of air and estimates the mean bubble diameter to be 1 mm. This is the equivalent of 80 cm^2 of bubble surface area per second. The water surface area bubbled was not given. Since the sample size was 4 l and since a laboratory glass frit was used; a bubble tube diameter of 10 cm does not seem to be an unreasonable approximation. A bubble surface area rate of $10^4 cm^2 m^{-2} sec^{-1}$ is calculated from these data, about four orders of magnitude greater than the open ocean value estimated by Wallace (1976). Even allowing for errors in these estimations, it appears that these experiments were carried out under conditions which would prevail only in severe storms.

The results of microlayer studies, BIMS studies, and aerosol samples discussed in this paper suggest that phosphorus injected into the atmosphere on sea salt particles is more likely to be surface-active organic material present in the sea surface microlayer rather than dissolved reactive phosphorus in the water column. This conclusion is supported by the work of Wallace (1976), who could find in foam floatation studies no evidence for the conversion of dissolved organic carbon to particulate organic carbon in sea water.

CONCLUSIONS

I have used a specially designed field sampler to confirm laboratory studies that suggested phosphorus was injected into the marine atmosphere on the drops from bursting bubbles. I have shown that this phosphorus is predominantly organic phosphorus, and that it is highly enriched relative to sodium compared to its concentration in the source water. Using the statistical techniques of factor analysis and regression analysis, I have shown that phosphorus from a marine source can be identified in the marine atmosphere over a phosphorus-rich upwelling area. Finally I have reviewed the evidence for the conversion of dissolved reactive phosphorus to a particulate organic form during the bubbling process. My conclusion is that the observed conversion could well be an artifact of the laboratory conditions used, and while the occurrence of such a process in nature is possible, the data to date suggest that it is not probable.

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ATMOSPHERIC PATHWAYS OF THE PHOSPHORUS CYCLE

ABSTRACT

Extensive measurements have been made of atmospheric phosphorus concentrations and deposition rates in marine and remote continental areas. This data, when combined with other published data on phsophorus deposition rates over the continents, have enabled the estimation of the atmospheric burden, the sources, the sinks, and the transfer rates of phosphorus through the atmosphere. I estimate that the total atmospheric burden of phosphorus is 2.8 x 10^9 g, 90% of which is over the continents. Deposition rates are calculated to be 321 x 10^{10} g y^{-1} of phosphorus onto the continents and 135 x 10^{10} g y^{-1} onto the surface of the ocean. Major sources of particulate phosphorus in the atmosphere are estimated to be: 1) soil particles containing both naturally occurring and fertilizer derived phosphorus - 397 x 10^{10} g y^{-1}, 2) phosphorus on sea salt particles - 33 x 10^{10} g y^{-1} and 3) phosphorus from industrial sources - 26 x 10^{10} g y^{-1}. The major sources of industrial phosphorus emissions are the phosphate industry - 15.6 x 10^{10} g y^{-1} and stationary combustion sources - 5.7 x 10^{10} g y^{-1}. A net flux of 102 x 10^{10} g y^{-1} of phosphorus is transported from the continents to the oceans through the atmosphere. Almost 50% of this transport is due to the flux of dust from the Sahara desert to the North Atlantic between 15° and 25° N. The input of phosphours which is easily soluble in sea water is estimated to be 22 x 10^{10} g y^{-1}. This value is about 10% of the input of dissolved phosphorus to the oceans by rivers.

INTRODUCTION

Phosphorus is an element vital to the life of all ogranisms from the smallest virus with its phosphorus containing ribonucleic acid (RNA), to the most complex large mammal with its calcium phosphate skeletal system, adenosine phosphate energy transport system, and deoxyribonucleic acid (DNA) and ribonucleic (RNA) processes for the storage, replecation, and transcription of genetic information. As such, phosphorus is an essential nutrient for both terrestrial and aquatic life, and it is often the nutrient controlling plant productivity.

Besides the importance of phosphorus to the growth and well being of all flora and fauna, the magnitude of the fluxes in the geochemical cycle of phosphorus can effect the behavior of the carbon and nitrogen cycles and, through the, the oxygen and sulfur cycles. Possible interrelationships between the phosphorus cycle and the nitrogen and carbon cycles have been discussed by Broecker (1973), Piper and Codispoti (1976) and Atlas (1976). The interaction of these cycles take place mainly in the oceans. The important fluxes, then, for the understanding of gross marine productivity and its effects on the cycles of other elements are those of dissolved phosphorus entering the ocean and all forms of phosphorus leaving the ocean.

Ecologists, agronomists, limnologists, and water quality chemists have recognized that the atmosphere can be a source of phosphorus and have included measurements of atmospheric phosphorus deposition in their nutrient budget, eutrophication and water quality studies (see, for example, Allen et al., 1968; Eaton et al., 1973; Gore, 1968; Johnson, 1966; Kluesever, 1972; Jones, 1960; Murphy, 1974; Pearson and Fisher, 1971; Schindler and Nighswander, 1970; Swank and Henderson, 1976; Turner et al., 1976; and Will, 1959, among others). From the standpoint of the phosphorus cycle, these studies can be viewed as investigations into subcycles of the main cycle.

Atmospheric fluxes of phosphorus have generally been omitted from published phosphorus cycles. Emery et al. (1955) in their estimation of the dissolved and particulate flux to the oceans assumed that rivers contributed all the input of phosphorus. Neither were atmospheric phosphorus fluxes in the cycles presented by Stumm (1973) and Lerman et al. (1975). Only Pierrou (1976) has presented a phosphorus cycle with an atmospheric component. Because of limited data, Pierrou could only estimate the annual rates of phosphorus deposition to the continents and to the oceans. No inputs of phosphorus to the atmosphere are presented, nor are any fluxes between the continents and the oceans given.

In this paper I will develop an atmospheric portion of the phosphorus cycle. I will use data I obtained on the atmospheric phosphorus content, sources, and deposition rates in marine and remote continental areas. In addition, I will use the published data or other investigators to assist me in building the continental portions of the cycle and in estimating the strength of crustal, marine, and anthropogenic phosphorus inputs to the atmosphere. I will also estimate the atmospheric phosphorus fluxes between the continental and oceanic regions of the earth. Because of scarcity of data in certain regions of the globe, and because of other assumptions that must necessarily be made, the cycle presented should be considered as only an estimate which is probably within a factor of 2 or 3 of the true values.

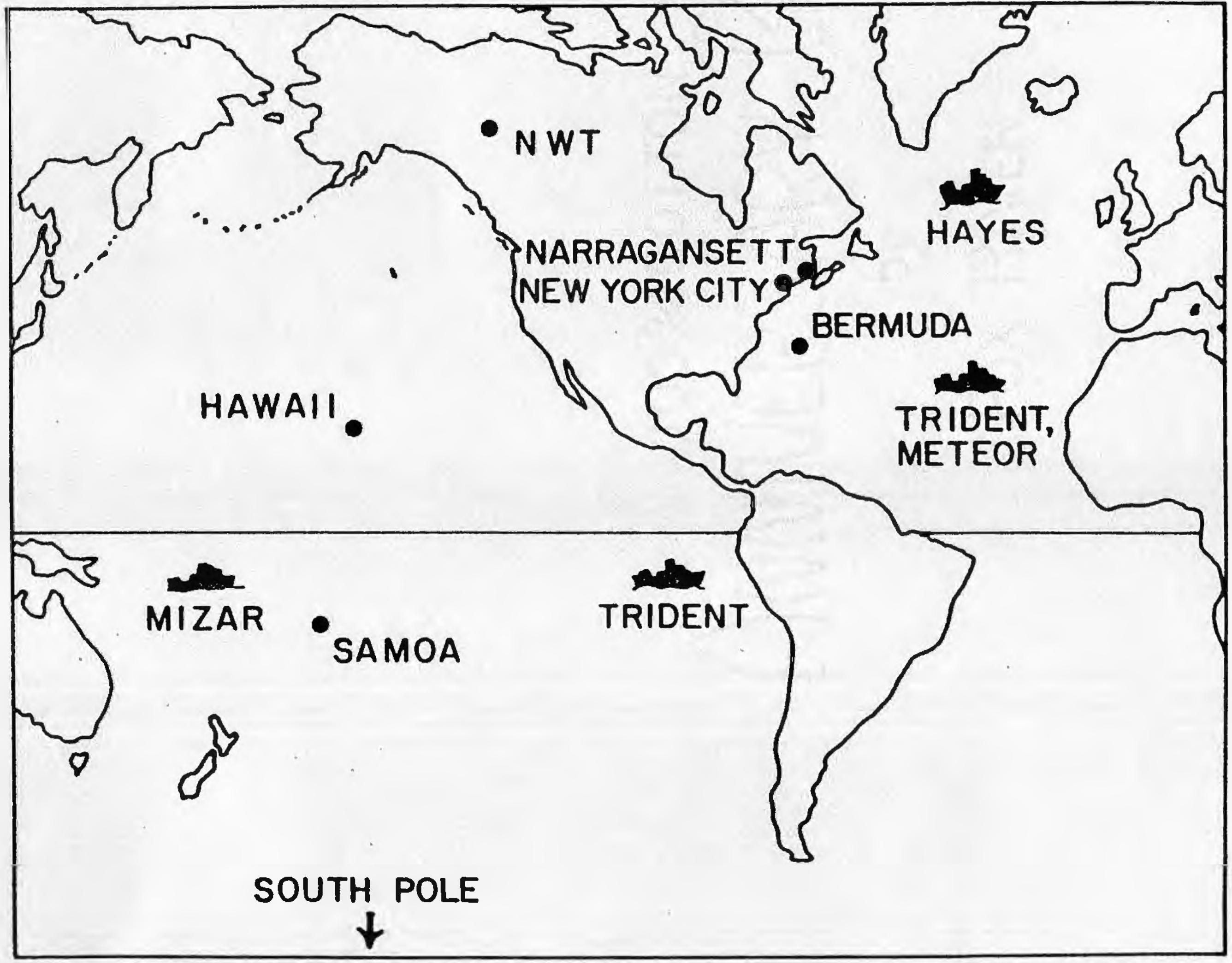
SAMPLING AND ANALYTICAL PROGRAM

I collected samples of atmospheric particulate matter over the North Atlantic between 1973 and 1975 on R/V TRIDENT cruises 134, 137, 145, 161, 168 and at an atmospheric sampling station located on the island of Bermuda. Additional samples were obtained from cruises of the R/V METEOR of the Federal Republic of Germany in the fall of 1973 and the USNS Hayes in the summer of 1976. Particulates in Pacific marine air were collected on TRIDENT cruise 165 along the coasts of Ecuador and Peru, at a Hawaiian sampling station between August and October 1975, and at a station in American Samoa in December, 1975 to February 1976 and again in June through October 1976. In addition, I received portions of aerosol samples collected by F.K. Lepple on a cruise of the USN Mizar during May and June of 1975.

Samples of atmospheric particulates from continental locations were collected at Narragansett, Rhode Island during 1975, at the Northwest Territories, Canada during February and March of 1975, and at the geographic South Pole between December and February 1975. I also received portions of two samples collected in New York City by K. Rahn in August, 1976. Fig. 1 illustrates my atmospheric sampling network.

The island sampling stations on Bermuda; Oahu, Hawaii; and Tutuila, American Samoa consist of 20m high sampling towers located on the windward sides of the islands. These towers are so situated as to sample prevailing trade winds. Samples of atmospheric particulates were collected on 20 x 25 cm Delbag Microsorban 97/99 filters using Cadillac

Fig. 1 Sampling sites and general cruise areas of the atmospheric phosphorus sampling program.



ATMOSPHERIC SAMPLING SITES
ATMOSPHERIC PHOSPHORUS STUDY

high volume sampling pumps. Delbag filters are reported to be 99% efficient for the removal of particles >0.3 μm in diameter (Dams et al., 1972). To prevent contamination of the samples by the pump exhaust, the pumps and auxiliary equipment were located three levels (6 m) below the filter holders. The Bermuda and Samoa sampling system contained wind direction and precipitation sensing units which shut down the system during periods of off-shore winds or rain. The Hawaiian sampling system was operated manually in a period of steady on-shore trade wind flow.

Filter samples were collected on the R/V TRIDENT using an atmospheric sampling tower mounted on the bow of the ship. Filter holders mounted on this tower were about 15 m above the ocean surface and were slightly forward of the bow. The filter holders were well in front of any bow spray. Samples from cruises 134, 137, and 145 were collected using double 20 x 25 cm Whatman 41 filters, while cruises 161, 165 and 168 used 20 x 25 cm Delbag Microsorban 97/98 filters. The efficiency of Whatman filters has been reported to be >90% efficient for the collection of particles >0.5 μm in diameter (Stafford and Ettinger, 1972). Sampling pumps were located below the filter holder to prevent contamination of the filters by pump exhaust. To prevent contamination by ship stack emissions, a directional air sampling control system was used. Sampling only occurred when the wind was ± 60° off the bow.

The Northwest Territory and South Pole samples were collected on Delbag filters using portable sampling units at these sites. Wind direction controllers were used at both sites to minimize local anthropogenic contamination of the samples. The New York City samples were collected on Whatman 41 filters on the top of the NYU Medical Building (15 stories) in Manhattan. The Narragansett, Rhode Island samples were collected manually on Delbag filters. The sampling equipment was located on the roof of the pump house belonging to the Environmental Protection Agency Marine Laboratory.

The volume of air sampled varied as to location. Sample air volumes ranged from 1000 m^3 (STP) in Narragansett and New York to 10,000 m^3 (STP) or more at the remote oceanic and polar sites.

After collection of the sample, the filter was quartered and the quarters stored in sealed polyethylene bags and frozen until analysis. Sodium, aluminum, and vanadium were determined by neutron activation. One quarter of the filter was pelleted and irradiated for 30 s in the Rhode Island Nuclear Science Center swimming pool reactor at a flux of 4×10^{12} n $cm^{-2}s^{-1}$. Within two minutes the samples were counted for 400 s on a 20 cm^3 Ge(Li) detector (resolution of 2.3 keV for the 1332 keV gamma ray of ^{60}Co, efficiency 7%) coupled to a Nuclear Data 2200 4096 channel analyzer with a computer compatible magnetic tape output (Ampex TM-7) for spectrum analysis. A computer program (J.L. Fasching, personal communication) was used to process the Ge(Li)spectra acquired. Absolute standards for each element were prepared on bank filters, pelleted, irradiated, and counted in the same manner as the unknowns. Constant geometry was maintained during the counting of all standards and unknowns. Corrections were made for dead time and half-life discrimination.

For total phosphorus analysis, two quarters of the filter were ashed individually at 550°C in the presence of excess magnesium. The residues were dissolved in 1 ml of 1 N HCl, diluted to 5 ml with doubly distilled (DD) water, and filtered through a 0.2 μm Nuclepore filter to remove insoluble particulates. The ashing beaker and filter were rinsed with two additional 5 ml aliquots of DD water, which was added to the original filtrate. After dilution of the filtrate to 40 ml, any arsenate present was reduced to arsenite by the method of Johnson and Pilson (1972). Phosphorus was then determined by the method of Murphy and Riley (1962). Corrections for filter blanks were made on all samples. Blank corrections ranged from 2-3% on the samples collected at Narragansett, R.I. to 25-30% on the samples collected in remote areas.

To determine the amount of atmospheric particulate phosphorus which is released upon contact with sea water, the filter samples were treated as follows: one quarter of a filter was added to a flask containing 40 ml of low phosphate (less than 0.1 μM) Sargasso Sea water. The sample was agitated for 30 minutes then stored for 12 hours in the dark. The sample was then filtered through a 0.4 μm Nuclepore filter and the phosphorus in the filtrate determined by the colorometric method of Murphy and Riley (1962).

Samples received from F.K. Lepple from the Pacific cruise of the USN Mizar were collected on glass fiber filters. These samples could not be ashed; instead they were added to a beaker with 40 ml DD water and then oxidized with 5 ml of a 6.4% potassium persulfate solution (Menzel and Corwin, 1965). Following filtration through a 0.4 μm Nuclepore filter, phosphorus was determined as above.

Analytical precisions were found to vary with the amount of material on the filter, precisions were poorer on filters collected in the remote areas where the concentration of many elements is extremely low. Typical analytical precisions were: total phosphorus, ± 10% to ± 15%; sodium ± 5% to ± 9%; aluminum ± 6% to ± 16%; vanadium ± 11% to ± 40%. Vanadium was undetectable on about one half the samples from Hawaii and all the samples from Samoa.

ATMOSPHERIC CONCENTRATION OF PARTICULATE PHOSPHORUS

Phosphorus over the continents

Concentrations of particulate phosphorus in ambient urban air are given in Table 1. Concentrations range from 30 to 1450 ng m^{-3}, and average about 150 ng m^{-3}. Concentrations appear to be somewhat higher in midwestern cities than in the east. This may represent higher dust loadings from agricultural activity in the midwestern United States. Industrial sources may also be important in some cities. Cincinnati, for example, is a major center for the manufacture of powdered detergents which, at the time the samples in Table 1 were collected, contained large amounts of inorganic phosphates.

There are fewer data available for non-urban locations. Delumyea and Petel (1977) measured the total phosphorus content of the air over southern Lake Huron. The average phosphorus content was 76 ng m^{-3}. I have measured the particulate phosphorus content of the air over a one-year period at a site in Narragansett, Rhode Island. Total phosphorus for this period averaged 19 ng m^{-3}, ranging from 10 ng m^{-3} in the winter months to 32 ng m^{-3} in the summer months (Table 2).

Perhaps the major sources of crustally derived atmospheric particulate material are the desert regions of the world. Some data are available which can be used to estimate the phosphorus concentration of the aerosol over the Sahara Desert. Lepple (1975) has measured the concentration of the Sahara dust from March to June, 1974 at a sampling site near the city of Nouadihibou, Mauritania. The average dust loading over this time was 830 µg m^{-3}. Based on one analysis, the phosphorus content of this dust was 0.11% (Lepple, personal communication). Using this value, the phosphorus content of the air at the Mauritanian sampling site is calculated to be

TABLE 1. PARTICULATE PHOSPHORUS CONCENTRATIONS IN URBAN AIR

LOCATION	PHOSPHORUS CONCENTRATION ng m^{-3}	REFERENCE
New York, NY	100 - 130	This paper
Denver, CO	100 - 200	Blosser (1970)
St. Louis, MO	100 - 200	Blosser (1970)
Washington, D.C.	30 - 100	Blosser (1970)
Philadelphia, PA	30 - 100	Blosser (1970)
Chicago, IL	100 - 300	Blosser (1970)
October 10, 1972	130 ± 48	Murphy (1974)
March 29, 1973	78 ± 23	Murphy (1974)
May 10, 1973	143 ± 80	Murphy (1974)
Urbana, IL	26 - 113[1]	Stein (1969)
Cincinnati, OH	50 - 300	Blosser (1970)
	220	Lee and Patterson (1969)
Fairfax, OH	310	Lee and Patterson (1969)
Los Angeles, CA	1450	Athanassiadis (1969)

[1] Orthophosphate only

$\sim$1000 ng m^{-3}, or almost an order of magnitude greater than the values for most urban areas. Since this site is in the center of the Sahara dust plume, the average phosphorus concentration in the atmosphere over other deserts of the world is probably a great deal less. While no data appear to be available for phosphorus in other desert regions, data for silica, calcium, and titanium in atmospheric particulate are available for Death Valley, California. A comparison can be made of the concentrations of the samples collected over Death Valley and over Scottsbluff, Nebraska by Blifford and Gillette as given in Cadle (1973). The near surface concentration in the desert regions are no more than a factor of two higher than those found in the great plains. This suggests that phosphorus concentrations over Death Valley might, in fact, be lower than over the plains due to the great amount of agricultural activity that occurs in the latter region. As far as the deserts of Asia are concerned, there are simply no data available.

Some limited data on atmospheric phosphorus have been obtained for two truly remote continental areas (Table 2). Aerosol samples collected in the Northwest Territories of Canada in the winter of 1975 average 1.3 ± 0.6 ng m^{-3} in total phosphorus content. Since biological activity is negligible and the ground is snow covered at this time of year, the atmospheric phosphorus in this region must be of local anthropogenic origin or transported to the site from other regions. Samples taken at even a more remote region, the geographic South Pole, average 0.21 ± 0.08 ng m^{-3} in total phosphorus. These values are the lowest continental values found. As every effort was made to avoid contamination of these samples by the local station emissions, this phosphorus was most likely transported to the Pole via long-range transport from other regions.

TABLE 2. PARTICULATE PHOSPHORUS CONCENTRATIONS IN NON-URBAN AIR

LOCATION	PHOSPHORUS CONC. ng m^{-3}	REFERENCE
Narragansett, R.I.	19 ± 8	This paper
Southern Lake Huron	74	Delumyea & Petel (1974)
Northwest Territories, Canada	1.3 ± 0.6	This paper
South Pole	0.21 ± 0.08	This paper

Phosphorus over the oceans

The concentrations of phosphorus in the marine air over the North Atlantic are shown in Figs. 2 and 3. Concentrations range over two orders of magnitude, with the highest values found adjacent to the North American and West African coasts. The lowest values appear to be in the upper North Atlantic. No data are available for the South Atlantic.

Concentrations of phosphorus in the air over the waters of the Pacific are shown in Figs. 4 and 5. The values in Fig. 4 represent the input of phosphorus from both continental and oceanic sources (this thesis, Chap. 5).

The phosphorus content of the marine air in the remote regions of the Pacific is very low even when compared to the North Atlantic values. Overall, the data suggest that by far the greater part of phosphorus in the marine atmosphere is from continental sources.

DEPOSITION OF ATMOSPHERIC PHOSPHORUS

Deposition onto the continents

There is a considerable body of data on the deposition of phosphorus onto land. Most of the data are in soil science or ecological journals. With the concern in recent years about eutrophication, more results are appearing in the water quality literature. This relatively large body of data is of uneven and often unknown quality. A variety of sample collection, sample storage, and analytical techniques have been used over the years. The bulk of the data are from what is generally called "bulk precipitation" and are collected over intervals which may vary from a few days to a month or more. Problems of sample contamination during collection and degradation during storage are considerable. In areas of intense biological activity, such as the tropics, contamination by insects is very

Fig. 2 Concentrations of atmospheric phosphorus in ng m^{-3} over the western North Atlantic. Data in ( ) represent range of values measured at Bermuda.

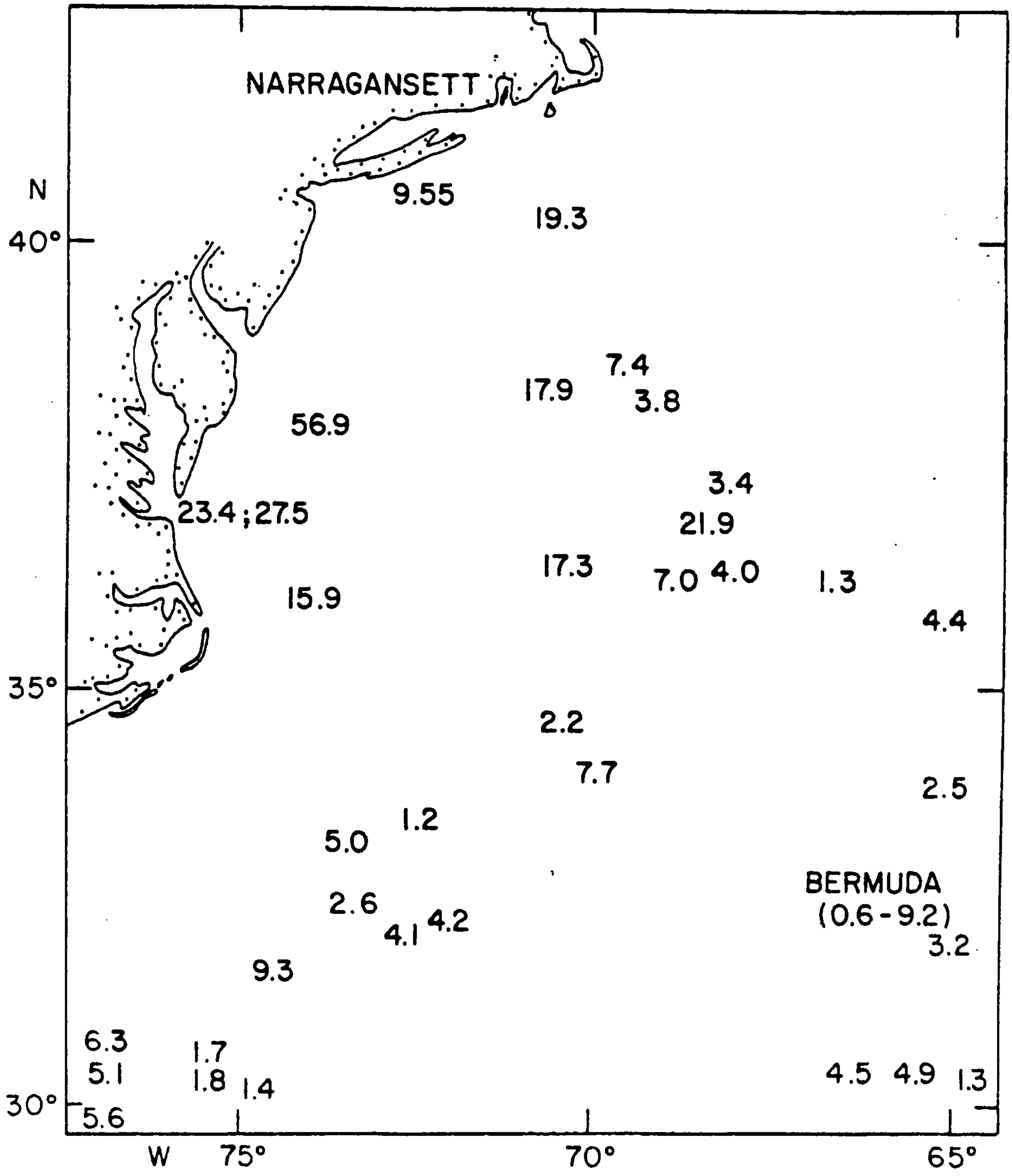

NARRAGANSETT
9.55
19.3
N
40°
7.4
17.9
3.8
56.9
3.4
23.4;27.5
21.9
17.3
7.0
4.0
1.3
15.9
4.4
35°
2.2
7.7
2.5
1.2
5.0
BERMUDA
(0.6-9.2)
2.6
4.2
4.1
3.2
9.3
6.3
1.7
5.1
1.8
1.4
4.5
4.9
1.3
30°
5.6
W
75°
70°
65°

Fig. 3 Concentrations of atmospheric phosphorus in ng m^{-3} over the North Atlantic.

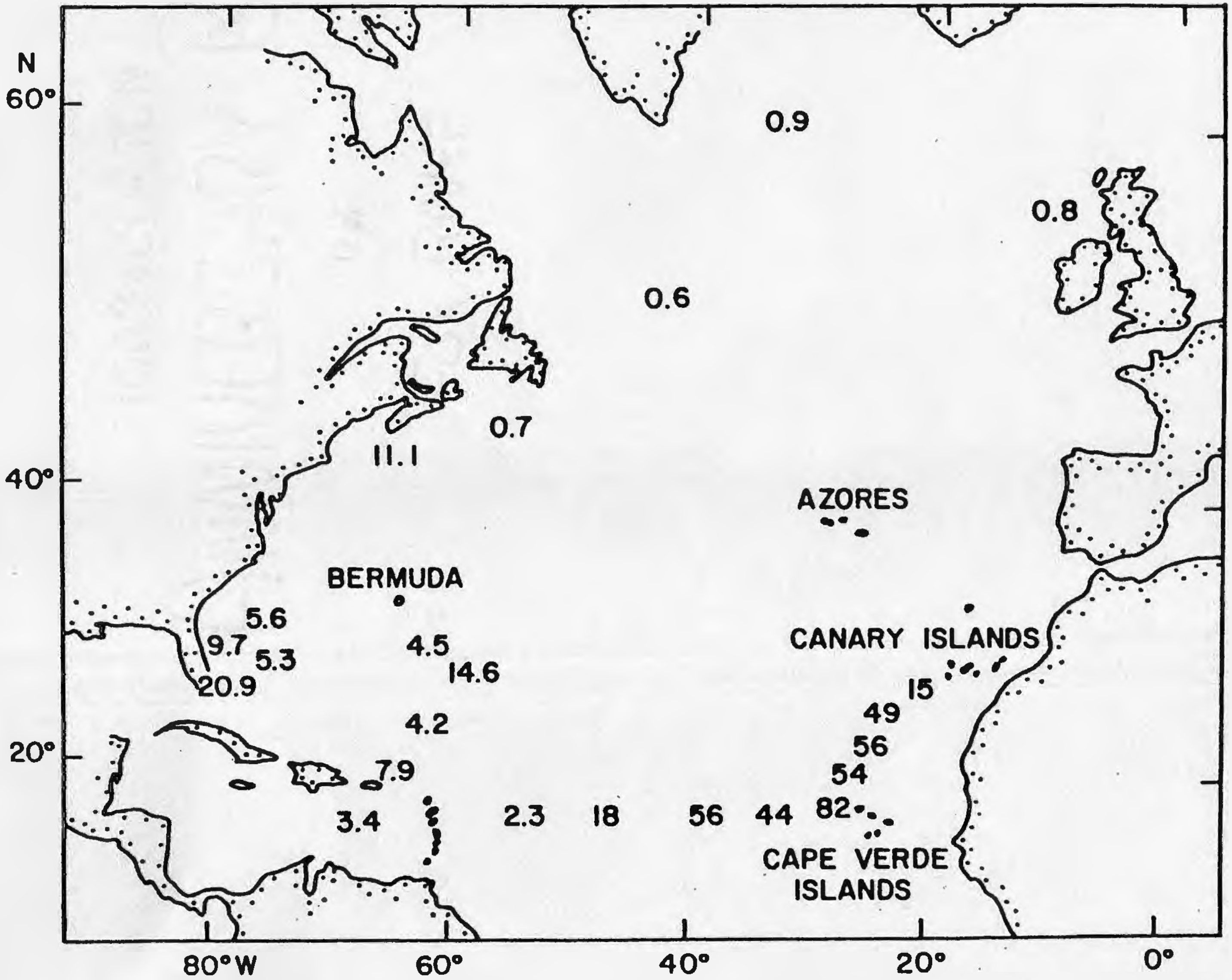

N
60°
40°
20°
80°W
60°
40°
20°
0°
0.9
0.8
0.6
0.7
11.1
AZORES
BERMUDA
5.6
9.7
5.3
20.9
4.5
14.6
4.2
7.9
3.4
2.3
18
56
44
82
54
56
49
15
CANARY ISLANDS
CAPE VERDE
ISLANDS

Fig. 4 Concentrations of atmospheric phosphorus in ng m^{-3} over the coastal waters of Peru and Ecuador on TRIDENT cruise 165.

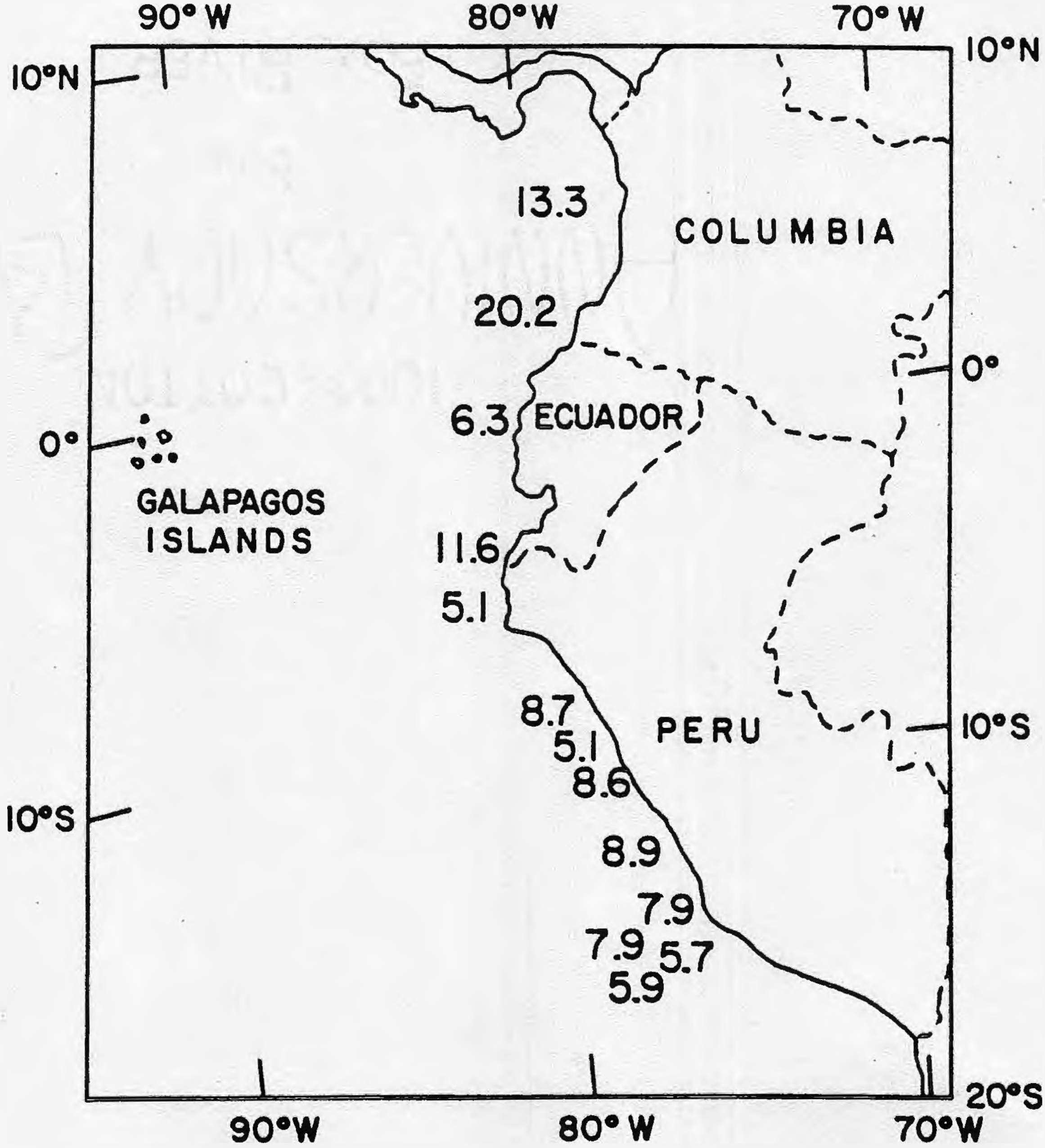
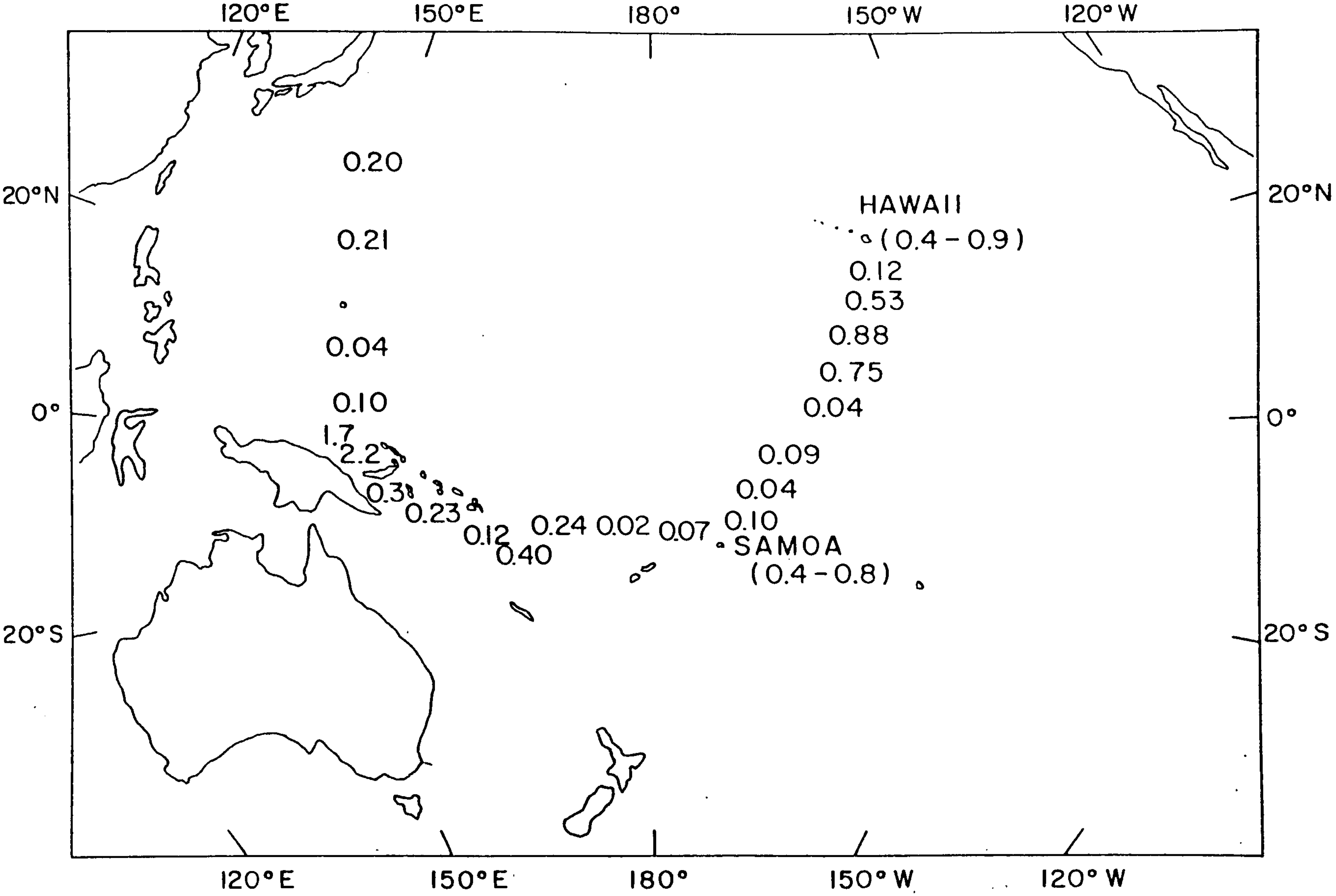

90° W
80° W
70° W
10°N
10°N
0°
0°
10°S
10°S
20°S
90°W
80° W
70°W
COLUMBIA
ECUADOR
PERU
GALAPAGOS ISLANDS
13.3
20.2
6.3
11.6
5.1
8.7
5.1
8.6
8.9
7.9
7.9
5.7
5.9

Fig. 5 Concentrations of atmospheric phosphorus in ng m^{-3} over the Pacific Ocean. Data in ( ) represent concentrations measured at the Hawaiian and Samoan islands.


120°E
150°E
180°
150° W
120° W
20°N
0°
20°S
0.20
0.21
0.04
0.10
1.7
2.2
0.3
0.23
0.12
0.40
0.24
0.02
0.07
0.10
0.04
0.09
0.04
0.75
0.88
0.53
0.12
HAWAII
(0.4 – 0.9)
SAMOA
(0.4 – 0.8)

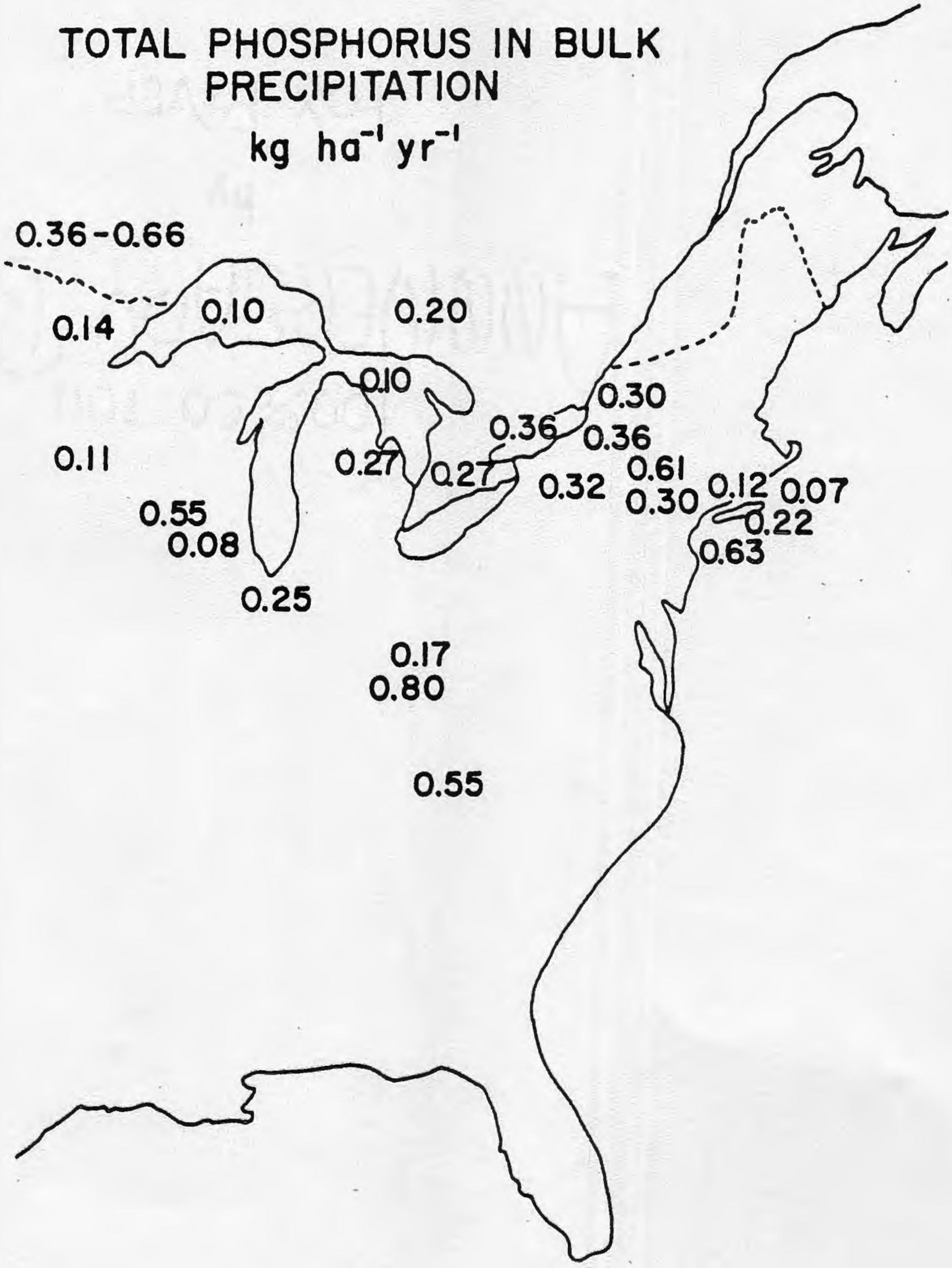
difficult to avoid (Ungemach, 1972). Bird feces are another major source of contamination. It seems likely that many of the very high values reported from tropical regions may be suspect for these reasons.

The data for Narragansett, R.I. from this study along with that reported by other investigators for the eastern portions of the United States and Canada are shown in Fig. 6 and given in more detail with references in Table 3. Deposition rates of total phosphorus range between 0.06 and 0.8 Kg ha^{-1} y^{-1}. High values are sometimes, but not always, associated with urban areas. The average deposition rate is about 0.3 Kg $ha^{-1}y^{-1}$. Much fewer data are available for the western United States and none for the arid regions of the southwest. The data that are published are given in Table 4. A high value is found for the urban area of Seattle, while the forested areas have deposition rates comparable to similar regions in the east.

A fair number of data points are available from the studies of European investigators. English and Swedish investigators have been particularly active in studies of the nutrient content of precipitation. The results of these European studies are given in Fig. 7 and Table 5. As in North America, a wide range of deposition rates are found. A comparison of average deposition rates indicates that concentrations of phosphorus in western Europe are about 60% higher than in North America ($\sim$0.5 Kg ha^{-1} y^{-1} vs $\sim$0.3 Kg ha^{-1} y^{-1}).

Some data are also available for other areas of the globe (Table 6). Three investigations in New Zealand found deposition rates similar to those in North America, as did a study in the Amazon River Basin of Brazil. Some very high values have been reported for parts of Africa and the Karala coast of India. One would like additional data from these locations

Fig. 6 Deposition rates of phosphorus from the atmosphere in North America (Kg $ha^{-1}y^{-1}$).



TOTAL PHOSPHORUS IN BULK PRECIPITATION

$kg\ ha^{-1}\ yr^{-1}$

TABLE 3. DEPOSITION OF TOTAL PHOSPHORUS IN THE EASTERN UNITED STATES AND CANADA

LOCATION	TOTAL P DEPOSITION Kg ha^{-1}y^{-1}	REFERENCE
Narragansett, RI	0.07	This paper
New Haven, CT	0.12[1]	Voight (1960)
Various locations in New York State	0.22 - 0.64	Pearson et al (1971)
Lake Ontario Basin	0.36	Shiomi and Kuntz (1973)
Lake Huron	0.10	Swanson (1976)
Southern Lake Huron	0.27	Delumyea and Petel (1977)
Lake Superior	0.10	Swanson (1976)
Northern Minnesota	0.14	Wright (1974)
Clear Lake, Ontario	0.27[1]	Schindler and Nighswander (1970)
Western Ontario	0.36 - 0.66	Schlinder et al. (1971) Schlinder et al (1973)
Sudbury, Ontario	0.20	Kramer (1973)
Cochocton, OH	0.17	Taylor (1971)
Cincinnati, OH	0.80[1]	Weibel (1966)
Chicago, IL	0.25	Murphy (1974)
Walkers Branch, TN	0.55	Swank and Henderson (1976)

[1] Calculated from precipitation analysis and annual rainfall

TABLE 4. DEPOSITION OF TOTAL PHOSPHORUS IN THE WESTERN UNITED STATES

LOCATION	PHOSPHORUS CONCENTRATION Kg ha^{-1} y^{-1}	REFERENCE
Seattle, WA	1.5	Johnson (1966)
Cedar River, WA	0.30	Turner et al.(1976)
Western Oregon	0.27	Fredrikson (1972)

Fig. 7 Deposition rates of phosphorus from the atmosphere in Europe (Kg $ha^{-1}y^{-1}$).

TOTAL PHOSPHORUS IN BULK PRECIPITATION

kg ha^{-1} yr^{-1}

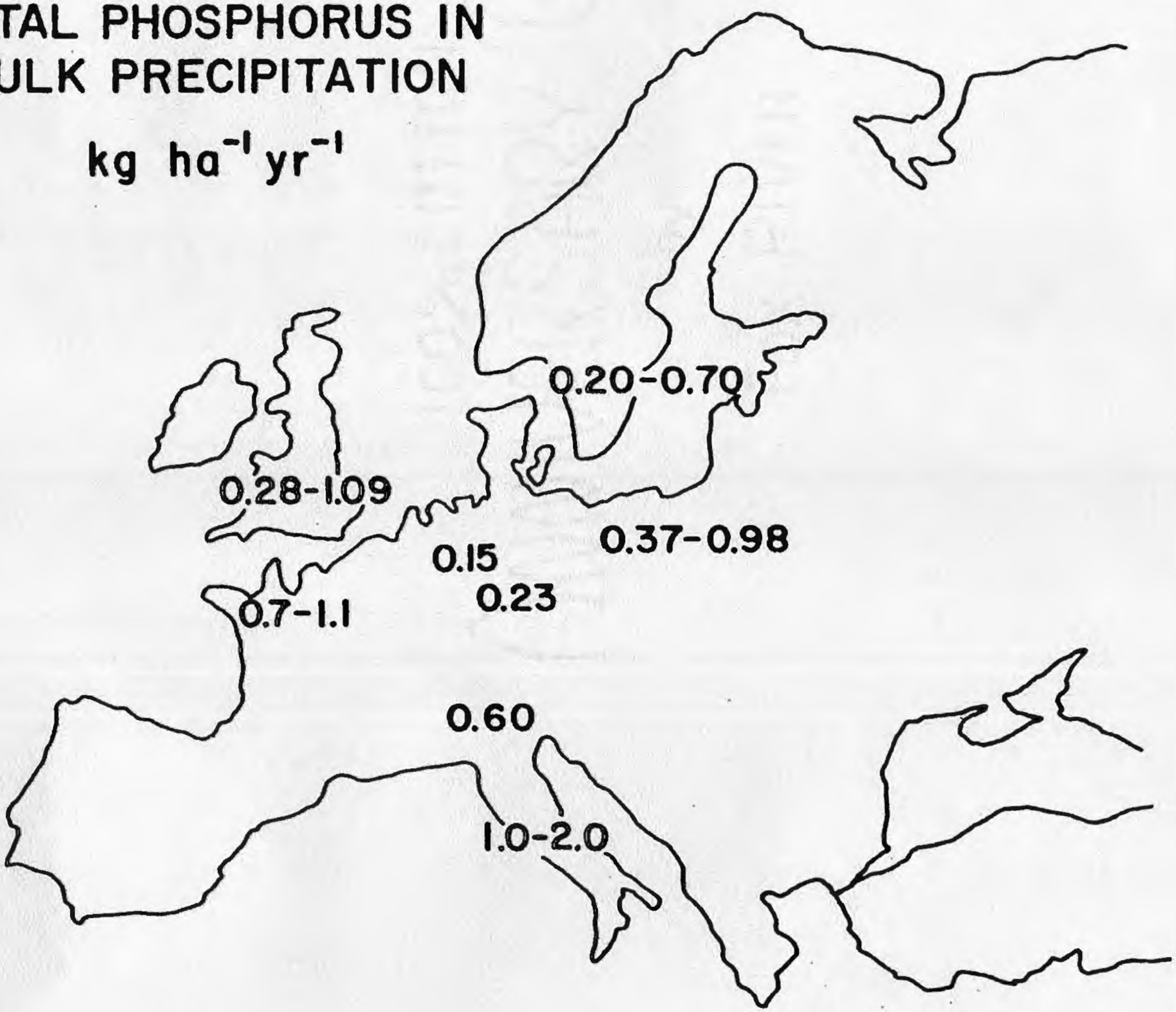


TABLE 5. DEPOSITION OF PHOSPHORUS IN WESTERN EUROPE

LOCATION	TOTAL PHOSPHORUS DEPOSITION Kg ha^{-1} y^{-1}	REFERENCE
Northwest England	0.30 - 1.0	Allen et al. (1968)
Yorkshire coast, England	0.80	Allen et al. (1968)
Kincardineshire, Scotland	0.20	Allen et al. (1968)
North Lancashire, England	0.43	Carlisle et al. (1966)
Lancashire, England	0.17 - 0.34	Goce(1968)
Lancashire, England	0.46	White and Turner (1970)
Near Stockholm, Sweden	∿0.20	Tamm (1951)
South Sweden	0.07[1,2]	Nehlgard (1970)
Sweden	.27	Pierrou (1976)
Sweden	0.70	Rigler (1974)
Dehlem, Germany	0.15[1]	Otterman (1965)
Gattwgen, Germany	0.23	Rupert (1975)
Sampling network over Poland	0.37 - 0.98	Chojnacki (1967)
Northwestern France	0.7 - 1.1	Rapp (1969)
Northern Italy	1 - 2	Gargano-Imperato (1964)
Czechoslovakia	0.04[1]	Chaliepa (1960)

[1] Inorganic soluble phosphorus only

[2] Calculated from concentration in precipitation and annual rainfall

TABLE 6. DEPOSITION RATE OF TOTAL PHOSPHORUS AT OTHER GLOBAL SITES

LOCATION	TOTAL PHOSPHORUS DEPOSITION Kg ha^{-1} y^{-1}	REFERENCE
North Island, New Zealand	0.28	Will (1959)
	0.22	Miller (1961)
	0.22	Egunjobi (1971)
Manaus, Brazil	0.29	Ungemoch (1972)
Northern Nigeria	2.6	Jones (1960)
The Gambia	0.14 - 0.28	Thornton (1965)
Natal Coast, South Africa	4.3	Ingham (1951)
Karala Coast, India	4.8	Vijayalkshmi and Panchalai (1963)

to confirm that the high deposition rates do indeed occur. For the present these values will be excluded from the averages used in later calculations.

Deposition onto the oceans

Data on the deposition rates of phosphorus onto the ocean surface are few. Graham (this thesis, Chap. 2) has estimated the deposition of atmospheric phosphorus on the Hawaiian and Samoan islands to be $\sim$0.03 Kg ha^{-1} y^{-1}. Total fallout samples were collected at Bermuda in the summer of 1974. A deposition rate of 0.06 Kg ha^{-1}y^{-1} is calculated from the phosphorus content of these samples. Profiles of atmospheric phosphorus concentrations over the North Atlantic as a function of distance from the North American continent yield deposition rates near the coast of 0.10 to 0.20 Kg ha^{-1}y^{-1}, while rates of 0.02 and 0.05 Kg ha^{-1}y^{-1} are estimated for locations 1000 Km offshore (this thesis, Chap. 4).

Two rain samples collected at approximately 32°N, 75°W between Bermuda and the U.S. coast contained an average of 6 μg P l^{-1} A sample collected in the Pacific at 3°N, 80°W contained 5.8 μgPl^{-1}, while a sample collected by Williams (1967) near Samoa was found to contain 2 μgPl^{-1}. If I assume an average annual depth of precipitation of 99.6 cm over the ocean (Barrington and Reichel, 1975), and a wet-to-dry deposition ratio of 2 to 1 (Blanchard, 1963), the equivalent deposition rates range between 0.03 and 0.09 Kg ha^{-1} y^{-1} for these three areas.

Deposition rates of dust fallout in the North Atlantic from the Sahara desert plume have been estimated by Lepple (1975) and Schütz (1977). Total input of dust near the coast ranges from 2300 to 37000 Kg ha^{-1}y^{-1} while approximately 30 to 40 Kg ha^{-1} y^{-1} fall on the ocean surface 500-2000 Km further west. Lepple (personal communication) has measured the total phosphorus content of a variety of aerosol samples collected near the coast. The phosphorus content of these samples averages 0.20%. Assuming these samples to be representative, total phosphorus inputs to the ocean range from 7 Kg ha^{-1} y^{-1} near the coast to 0.05 Kg $ha^{-1}y^{-1}$ at a distance of 500 to 2000 Km from the coast.

No data appear to be available to enable the estimation of phosphorus deposition rates in the North Pacific, where an input of dust from the Asian deserts may occur.

ESTIMATION OF ATMOSPHERIC BURDEN OF PHOSPHORUS

As shown above, many more data are available for the deposition rates of phosphorus over continents than for the continental concentrations of atmospheric particulate phosphorus. Consequently I can arrive at a better estimate of the atmospheric phosphorus concentration from the available data on deposition rates than from the few available concentration measurements. To arrive at an average atmospheric phosphorus concentration over the continents, I must estimate a deposition velocity for the continental phosphate aerosol.

Junge (1963) has defined the deposition velocity as $V = D/C$ where D is the rate of deposition and C is the air concentration. The total deposition rate is given by $D_t = D_p + D_s + D_i$ where the subscripts p, s, and i refer to precipitation, sedimentation and impaction respectively. The overall deposition velocity, then, is $V_t = V_p + V_s + V_i$.

I can estimate V_t for sites where I have values for D_t and C. I have these values for four sites, two urban and two rural. The values of V_t calculated from this data are given in Table 7. The average V_t is ~ 1 cm sec^{-1}.

TABLE 7. TOTAL DEPOSITION VELOCITIES CALCULATED FROM DEPOSITION RATES AND ATMOSPHERIC PHOSPHORUS CONCENTRATIONS

LOCATION	ATMOSPHERIC PHOSPHORUS CONCENTRATION ng m^{-3}	PHOSPHORUS DEPOSITION RATE - Kg ha^{-1} k^{-1}	DEPOSITION VELOCITY cm s^{-1}
Narragansett, RI[1]	19	0.06	1.00
Southern Lake Huron[2]	74	0.24	1.03
Chicago, IL[3]	120	0.25	0.67
Cincinnati, OH[4]	220	0.80	1.16
		Average	0.97

---

[1] This study

[2] Delumyea and Petel (1977)

[3] Murphy (1974)

[4] Weibel et al. (1966)

For purposes of estimating the average atmospheric phosphorus concentration over the continents, I have used average annual deposition rates of 0.3 Kg $ha^{-1}y^{-1}$ for North America, 0.5 Kg ha^{-1} y^{-1} for Europe, and a value of 0.25 Kg $ha^{-1}y^{-1}$ for the rest of the continental areas. I have used a deposition velocity of 1 cm s^{-1}. With these assumptions, the weighted average continental phosphorus concentration is estimated to be 90 ng m^{-3} (Table 8).

Scale heights are commonly used in describing atmospheric properties which decrease exponentially with altitude. The scale height represents the height at which 1/e or ∿37% of the initial value of a property remains. For an isothermal atmosphere the scale height represents the height at which 1/e of ∿37% of the initial pressure remains (Tverskoi, 1965). Scale height can also be expressed as the height the atmosphere would have were it compressed to a constant density (Tverskoi, 1965). As this homogeneous atmosphere is a subset of an isothermal atmosphere, the two definitions yield identical scale heights. Aerosols over the continents appear to have scale heights of 1-2 Km up to about 4 Km altitude (Junge, 1963; Shaw, 1975). Silica, calcium, and titanium profiles with altitude measured over the great plains of the United States yield similar scale heights (Gillette and Blifford, 1971). Above 4 Km, the concentrations of the elements are reasonably constant up to the highest altitude sampled, 9 Km. The behavior over desert regions is considerably different, however. Over Death Valley, the concentrations of these elements were much more constant with altitude, and scale heights appear to be more on the order of 4 Km with constant concentrations above 6 Km (Gillette and Bifford, 1971). This shows the effect of the strong convective heating which occurs over desert regions.

TABLE 8. WEIGHTED AVERAGE CONCENTRATION OF ATMOSPHERIC PHOSPHORUS OVER THE CONTINENTS

CONTINENT	DEPOSITION RATE Kg ha^{-1} k^{-1}	CALCULATED ATMOSPHERIC CONCENTRATION ng m^{-3}	PERCENT OF GLOBAL LAND MASS	FRACTIONAL CONTRIBUTION
North America	0.30	100	14%	14
Europe	0.50	150	6%	9
Rest of Continents	0.25	80	84%	67
			Weighted Average ng m^3	90

My assumptions, then, for calculating the atmospheric burden of phosphorus over the continents are as follows:

1. The average concentration of phosphorus in the atmosphere is 90 ng m^{-3} between 60°N and 60°S. Based on the values measured in the Northwest Territories and in Antarctica, I assume a value of zero between 60° and the poles,

2. The aerosol scale height over non-desert regions (80% total land area) is 1.5 Km, up to an altitude of 4 Km. Using a value of 90 ng m^{-3} for the phosphorus concentration at ground level, the concentration of phosphorus at 4 Km is then 6 ng m^{-3}. I assume a constant concentration of 6 ng m^{-3} between 4 and 11.3 Km.

3. The aerosol scale height over desert regions (20% of total land area) is 4 Km up to an altitude of 6 Km. Assuming 90 ng m^{-3} at the surface, the phosphorus concentration at 6 Km is then 20 ng m^{-3}. I assume this concentration to be constant between 6 and 11.3 Km.

4. The land area between 60°N and 60°S is 1.17 x $10^8 Km^2$ (Baumgartner and Reichel, 1975).

Based on these assumptions, the burden of atmospheric phosphorus over the continents is estimated to be 2.5 x 10^{10}g,

In calculating the burden of phosphorus over the oceans, I make the following assumptions:

1. The average concentration of atmospheric phosphorus over the North Atlantic between 25 and 45°N is 6 ng m^{-3}. Above 45°N it is 1 ng m^{-3}. Between 15°N and 25°N it is calculated to be 57 ng m^{-3} from the coast of Africa to 40°W, while a value of 6 ng m^{-3} is used between 40°W and the Caribbean. Below 15°N, a value of 1 ng m^{-3} is assumed.

2. The average concentration of phosphorus over the other oceans

of the world is 1 ng m^{-3}. While this is higher than the values measured in the remote Pacific, I have no samples from the regions of the North Pacific where the prevailing westerlies can carry Asian dust as far as Alaska (Rahn, personal communication).

3. Using the profiles of Gillette and Blifford (1971) over the Pacific Ocean, I assume a scale height of 0.9 Km up to 1 Km, and constant concentration of 33% of the surface phosphorus from that height to the tropopause. An exception is made for the area of the ocean under the Sahara plume. Here I assume a constant concentration between 0 and 5 Km, and no phosphorus above 5 Km. The relatively constant concentration in the lower levels of the troposphere results from the intense convective heating over the desert (Schütz, 1977). Thus the aerosol is transported high into the troposphere before being swept out over the oceans. I will assume this constant concentration to exist from the African coast to 40°W.

With these assumptions, I obtain a burden of phosphorus over the oceans of 3.0 x 10^9 gms, or about 12% of the burden over the continents. The total global burden of phosphorus then is estimated to be 2.8 x 10^{10}g.

GLOBAL DEPOSITION OF PHOSPHORUS FROM THE ATMOSPHERE

The calculation of the estimate of the annual deposition of phosphorus over the globe is shown in Table 9. The continental deposition rates used in these calculations are those used previously for the burden calculation. For calculation of deposition onto the oceans, I have chosen to use a value of 0.04 Kg $ha^{-1}y^{-1}$ for the North Atlantic and 0.02 Kg $ha^{-1}y^{-1}$ for the other oceans of the world. To the deposition total calculated for the Atlantic using a 0.04 Kg ha^{-1} deposition rate I add 50 x 10^6g,

TABLE 9. CALCULATION OF THE ANNUAL DEPOSITION OF PHOSPHORUS OVER THE GLOBE

AREA	DEPOSITION RATE Kg ha^{-1} y^{-1}	SURFACE AREA[1] 10^{6} Km	TOTAL DEPOSITION 10^{10} g	
North America	0.30	16.719[2]	50	
Europe	0.50	7.436[2]	37	
Other continental	0.25	93.466[3]	234	
Total continental		117.621		321
North Atlantic	0.04	52.264	73[4]	
Other oceanic	0.02	308.846	62	
Total oceanic		361.110		135
Total global				456

[1] Data of Baumgartner and Reichel (1975)

[2] Excludes land area north of 60°N

[3] Excludes land area north of 60°N and Antarctica

[4] Includes 52 x 10^{10}g y^{-1} from the Sahara desert.

representing the input of phosphorus from the Sahara plume. It is possible that there are other highly localized atmospheric inputs of phosphorus to the oceans, especially from other desert regions of the globe. However, the data are simply not available from these regions.

SOURCES OF ATMOSPHERIC PHOSPHORUS

Phosphorus may be injected into the atmosphere on soil particles as a result of erosion by wind, in the spores, fungi, and pollen that result from biological activity, on sea salt particles derived from the oceans, and as emissions due to man's industrial and agricultural activities. The industrial emissions are the most easily estimated. Concerns over air quality deterioration in recent years have led to the compilation of data on phosphorus emissions or on the phosphorus content of emissions. The amount of phosphorus injected on sea-salt particles is more difficult to estimate. However, sufficient data are available to enable a reasonable approximation to be made. An estimate of the amount of phosphorus carried into the atmosphere on terresterially derived material is the most difficult to derive directly due to the multiplicity of mineral and biological sources of terrestrial phosphorus, and the wide range in the published estimates of the global dust flux.

Anthropogenic inputs of phosphorus

Both agricultural and industrial activity contribute to anthropogenic phosphorus emissions into the atmosphere. Soil particles containing phosphorus are injected into the atmosphere during agricultural and construction activity, and by the passage of vehicles over unpaved roads. Bryson (1974) has estimated that 100 - 250 x 10^{12} g y^{-1} of soil particulates are injected into the atmosphere on a global basis. Farmland in the United

States averaged 0.065% phosphorus in the top soil in 1936 (Black, 1968). Phosphorus concentration in soil tend to be highest in the finest fractions (Black, 1968). Soil which has been fertilized regularly accumulates phosphorus; a soil in England which had been fertilized over 100 y contained 0.13% phosphorus, 2.5 times the amount found in the untreated soil.

Statistical techniques can be used to estimate the percentage of phosphorus present in crustal or soil-derived material collected in aerosol samples. In addition to the determination of phosphorus in my aerosol samples, I have determined the elements aluminum, sodium, and vanadium. Aluminum serves as a tracer for soil or crustal material, sodium as a tracer for sea salt, and excess vanadium above that which is crustally derived as a tracer for inputs from fossil fuel combustion sources. I have analyzed the Narragansett, R.I. sample set by statistical techniques using these tracers. Multi-variate linear regression of phosphorus against these three tracers shows a significant regression of phosphorus against aluminum. The aluminum coefficient of the regression equation is 0.012 ± 0.003. The regression on aluminum is highly significant (0.9996) but only explains 27% of the sample variation. The high unexplained variance is probably due to biological and anthropogenic phosphorus inputs into the aerosol which are not separable statistically. So while the assumption of a simple linear relationship is clearly an oversimplification, it does provide me with an estimate of the phosphorus present in soil and crustal material in the atmosphere. The ratio of phosphorus to aluminum of 0.012 ± 0.003 is in good agreement with the ratio of phosphorus to aluminum in rock and soils. Estimates of this ratio range from 0.009 to 0.015, with an average of 0.012 (Rahn, 1976). Aluminum comprises about 8% of rocks and about 7.1%

of soils (Rahn, 1976). I assume an average aluminum concentration in the aerosol of 7.5%. Thus the percentage of phosphorus in continental dust at Narragansett is estimated to be 0.09 ± 0.03%. This range of values appear to be in reasonable agreement with the literature values for soil phosphorus previously discussed. I assume soil to contain 0.1% phosphorus. Between 10 and 25 x 10^{10} g y^{-1} are estimated to be injected into the atmosphere on soil particles by man's activities. A value of 20 x 10^{10} g y^{-1} will be used in this paper.

Approximately 0.1 x 10^{12}g y^{-1} of particulate matter are emitted in the United States annually by the burning of agricultural refuse (EPA, 1976). Land under cultivation in the United States comprises about 35% of the world total (Compton's Encyclopedia, 1971). The global emissions from agricultural burning are estimated to be 0.3 x 10^{12}g y^{-1}. Emissions from agricultural burning are estimated to contain 0.15% phosphorus (Murphy, 1974). Phosphorus emissions on this basis are about 4.5 x 10^{8} g y^{-1}.

The major sources of industrial emissions of phosphorus are the mining of phosphorus rock and the manufacture of fertilizer. U.S. emissions of phosphorus by the phosphorus industry are estimated to be 4.5 x 10^{10} g y^{-1} for the year 1970 (EPA, 1973). Because of increases in rock production, I estimate emissions to have increased to 5.8 x 10^{10}g y^{-1} by 1974 (Stowasser, 1974). Global emissions of the phosphorus industry are thus estimated to be 15.6 x 10^{10} g y^{-1}.

Other major sources of industrial emissions of phosphorus are stationary combustion processes. U.S. emissions of phosphorus from coal combustion are estimated to be 0.8 x 10^{10}g y^{-1} (EPA, 1973). Coal emissions in the U.S. amount to between 6 and 6.5 x 10^{12}g y^{-1} (Vandegrift and Shannon, 1971; Cavender et al., 1973). This is about 14% of the global emissions from coal burning (Robinson and Robbins, 1971). Global phosphorus emissions from coal combustion are estimated to be 5.7 x 10^{10} g y^{-1}.

Domestic emissions of phosphorus from the iron and steel industry amount to 0.25 x 10^{10} g y^{-1} (EPA, 1973). Emissions from this industry in the U.S. amount to 1.4 x 10^{6}T y^{-1}, or 17% of the global total (Vandergrift and Shannon, 1971; Cavender, 1973; Robinson and Robbins, 1971). Based on these figures, global phosphorus emissions from the iron and steel industry are 1.5 x 10^{10}g y^{-1}.

Pierrou (1976) has provided a macabre estimate for emissions of 2 x 10^{9}g y^{-1} of phosphorus from the cremation of human bodies.

Other industrial emissions of phosphorus have been estimated using the global particulate emission rates of Robinson and Robbins (1971) multiplied by an appropriate phosphorus concentration. These estimates are given in Table 10. The global anthropogenic inputs of phosphorus are summarized in Table 11.

In addition to the phosphorus released during the burning of agricultural fields, naturally occurring and man-made forest fires also emit particulate phosphorus to the atmosphere. About 0.6 x 10^{12}g y^{-1} of particulates are emitted annually in the United States by forest wildfires and forest managed burning (EPA, 1976). As the United States contains about 10% of the world's forests (Compton's Encyclopedia, 1971), I assume 6 x 10^{12} g y^{-1} to be emitted globally. Other estimates range from 3 x 10^{12} to 150 x 10^{12} g y^{-1} (Robinson and Robbins, 1971). Murphy (1974) suggests using 0.1% as the phosphorus content of forest fire particulates. Assuming this percentage, I estimate that 0.6 x 10^{10}g y^{-1} of phosphorus are injected into the atmosphere by forest fires. While it is not always possible to identify the causes of forest fires, many if not most are caused by man's activities.

TABLE 10. MINOR POLLUTANT EMISSION SOURCES OF PARTICULATE PHOSPHORUS

SOURCE	GLOBAL PARTICULATE EMISSIONS[1] 10^{12} g y^{-1}	% PHOSPHORUS	PHOSPHORUS EMISSIONS 10^{10}g y^{-1}
Cement	6.5	0.026[2,3]	0.17
Lime Production	2.6	0.66[3]	0.17
Fuel Oil Combustion	0.32	0.40[4]	0.13
Residual Oil Combustion	0.81	0.40[4]	0.32
Incineration	4.25	0.10[5]	0.43
Noncommercial Fuel	7.70	0.10[5]	0.77

[1] Robinson and Robins (1971)

[2] Vandergrift and Shannon (1971)

[3] Riley and Skirrow (1975).

[4] Smith (1962). Residual oil assumed the same as fuel oil

[5] Assumed the same as for pure wood (Murphy, 1974)

TABLE 11. ESTIMATED GLOBAL ANTHROPOGENIC EMISSIONS OF PHOSPHORUS

SOURCE	ANNUAL EMISSION RATE 10^{10}g
Phosphate manufacture	15.6
Coal combustion	5.7
Iron and steel manufacture	1.5
Cement manufacture	0.2
Lime manufacture	0.2
Fuel oil combustion	0.1
Residual oil combustion	0.3
Non-commercial fuel	0.8
Incineration	0.4
Forest wildfires and controlled burning	0.6
Agricultural burning	0.05
Cremation	0.2
	25.7
Soil from man's activities	∿20
	∿46

Therefore, forest fire emissions have been shown with other anthropogenic emissions in Table 11.

Inputs from volcanoes

It is quite possible that inorganic phosphates are volitalized at high temperatures and emitted by volcanic activity. However nothing is known about the emission of volatile phosphorus compounds during volcanic activity and no estimate of phosphorus emissions from this source can be made.

Oceanic inputs of phosphorus

Sea salt particles comprise a major portion of the particulate matter present in the lower troposphere (Robinson and Robbins, 1971). Two major studies have provided estimates of the annual flux of sea salt through the atmosphere. Eriksson (1959, 1960) estimated the annual production of sea salt particles to be 10^{15}g y^{-1}. Blanchard (1963) arrived at a value one order of magnitude greater, 10^{16}g y^{-1}.

When droplets of ocean water are ejected into the atmosphere by bursting bubbles, chemical fractionation processes can occur. Phosphorus is an element which was found to be enriched, i.e., the P/Na ration on the sea salt particle is higher than the P/Na ratio in the source sea water. Phosphorus enrichment has been found on particles generated by the bubbling of sea water in the laboratory (MacIntyre and Winchester, 1968), in a field study in Narragansett Bay, R.I., and in marine aerosol samples collected over the upwelling zones near the Peruvian coast (this thesis, Chap. 5). Enrichments typically range from 10 to 200.

Multivariate linear regression analysis has been applied to the phosphorus data obtained at the Hawaiian and Samoan sampling sites and to the data obtained off of the coast of Peru. Regression coefficients of phosphorus against sodium were found to be $(0.7 \pm 0.2) \times 10^{-4}$ for the remote island samples and $(5.7 \pm 1.3) \times 10^{-4}$ for the Peruvian coastal water samples. Both coefficients were significantly different from zero at a 99% confidence level. The average concentration of total phosphorus in the Peruvian surface waters at the time the aerosol samples were collected was 1.2 μM l^{-1}. The surface waters upwind of the Hawaiian and Samoan islands contain less than 0.25 μM l^{-1} of reactive phosphorus (Reid, 1962). I assume that the concentration of total phosphorus in these surface waters is similar to nutrient poor regions of the Sargasso Sea. Total phosphorus in these surface waters averages about 0.15 μM l^{-1} (Pilson and Kester, unpublished data). The regression coefficients of phosphorus against sodium are assumed to be representative of the ratio of marine phosphorus to sodium in the aerosol. Using these ratios and the surface water phosphorus concentrations discussed above, I estimate the enrichment of phosphorus in the marine aerosol to be ∿170 near Peru and ∿160 at the remote island sites. An average of 165 is used in the calculations to follow.

The average surface water total phosphorus content of the Atlantic Ocean between 60°N and 40°S has been calculated from the station data available for the IGY cruises (Worthington, 1959; Metcalf, 1960; Miller, 1960; Metcalf, 1958; Worthington, 1958; Fuglister, 1957). The average value of the total phosphorus at 178 stations is 0.4 μM l^{-1}. The average reactive phosphate level is calculated to be 0.2 μM l^{-1}, or 50% of total phosphorus. The average value of 0.4 μM l^{-1} for total phosphorus does not include any contribution from the rich Antarctic waters. Baleck et al. (1968) indicate that the reactive phosphorus content of these waters ranges from 1 to greater than 2 μM l^{-1}. I assume that the waters from 50-60°S contain 2μM l^{-1} total phosphate. The area between 50-60°S comprises 7% of the total area of the Atlantic between 60°S and 60°N (Baumgartner and Reichel, 1975). Including the phosphorus in these waters raises the average value for the Atlantic to 0.5 μM l^{-1}.

The maps of Reid (1962) were used to estimate the phosphorus in the surface waters of the Pacific. A weighted average reactive phosphorus value of 0.43 $\mu M\ l^{-1}$ was calculated from these maps. If I assume the concentration of organic phosphorus equals that of reactive phosphorus, I obtain a value of 0.86 $\mu M\ l^{-1}$ as an average total phosphorus content of Pacific waters.

The Pacific is about twice the Atlantic in area. On this basis I calculate an all ocean average of total phosphorus in surface waters to be 0.74 $\mu M \cdot l^{-1}$. Applying our enrichment factor of 165, I obtain a ratio of phosphorus to sodium in sea salt of 3.5×10^{-4}. Assuming 31% sodium in sea salt particles, this is equivalent to the phosphorus concentration of 0.01% on a dry particle basis. Applying this concentration to the estimates of Ericksson (1959, 1960) and Blanchard (1963) yields an input of phosphorus to the atmosphere of from 10 to 100 x 10^{10} g y^{-1}.

Crustal aerosol inputs

A major problem is estimating the input of crustal phosphorus to the atmosphere. The total input of crustal material to the atmosphere is very poorly known, with a wide range of estimates available. Estimates for the amount of windblown dust derived from the continents has been presented in the SCEP Report (1970), by Peterson and Junge (1971) and by Robinson and Robbins (1971). Some estimates consider fine particles only, while others consider all sizes of airborne particles. Thus the estimates vary widely. At the lower end of the range is the estimate of 70 x 10^{12} g y^{-1} based on the dust fall rate in glacial sediments. This is an estimate for fine particles only. Peterson and Junge (1971) site an estimate by Goldberg (personal communication to the authors) of 500 x 10^{12} g y^{-1}. This estimate was derived from deep-sea sediments and again should be considered an estimate of fine particle dustfall. Additional dustfall estimates given in Peterson and Junge (1971) are 250 x 10 g y^{-1} for particles less than 5 μm in diameter and 500 x 10^{12} g y^{-1} for particles of all sizes. Robinson and Robbins (1971) assumed dust concentrations and aerosol residence times for dust over the continents and over the oceans. From these data they calculate an input of continental dust to the atmosphere of 200 x 10^{12} g y^{-1}.

Recent studies on the transport of Sahara dust to the waters of the North Atlantic suggest that the above estimates may all be low in that they underestimate the total amount of crustal material of all sizes in the global atmosphere. The glacial ice and deep-sea sediment studies reflect only the deposiiton of fine particles which were transported long distances from their source regions. Robinson and Robbins (1971) rely heavily on reported measurements of dust concentrations using the mesh technique. This technique has been shown to underestimate dust loading in the atmosphere by factors of 3 to 10 (Goldberg, 1971; Prospero and Nees, 1977). Two recent investigations have concluded that transport of dust particles less than 40 m diameter from the Sahara desert alone is approximately 250 x 10^{12} g y^{-1} (Lepple, 1975; Schütz, 1977). Schütz (personal communication) has estimated that 1000 c 10^{12} g y^{-1} of dust may be injected into the atmosphere over the Sahara, while the global value may range from 2000-4000 x 10^{12} g y^{-1}.

Soil samples on the Northwest coast of Africa contain an average of 0.13% phosphorus, while aerosol samples collected off the Africa coast have shown an average of 0.2% (Lepple, personal communication). I have analyzed the fine fractions (16 µm radius) of the Libyan desert, much further to the east. These samples contained only 0.07% phosphorus. Thus the phosphorus content of the Sahara plume may be strongly influenced by the presence of large apatite deposits in western North Africa and may not be representative of the total Sahara aerosol. As discussed in the section on anthropogenic inputs, soil from the North American continent and from England appear to contain about 0.1% phosphorus. For these calculations, a value of 0.1% for the crustal aerosol is assumed.

Applying this percentage to the annual deposition of phosphorus over the continents results in an estimate of 3000 x 10^{12} g y^{-1} of dust input to the atmosphere. This of course assumes that all the phosphorus deposited is associated with crustal material in one way or another.

If I assume that the dust contains 0.2% phosphorus as found in the Sahara plume, I obtain an input of dust to the atmopshere of 1600 c 10^{12} g y^{-1}. Reversing this calculation by applying the percentage of phosphorus in crustal material to the earlier estimates of dust in the atmosphere gives input values of 7 to 500 x 10^{10} g y^{-1} at the 0.1% phosphorus level or twice that at the 0.2% level in dust.

This is not nearly enough phosphorus to account for the calculated deposition over the globe and suggests that much of the phosphorus deposition may be large particle and that the higher estimates of the amount of crustal particulates of all size ranges present in the global atmosphere may be more accurate. In this paper I assume an input that balances the deposition of crustal phosphorus over the globe. As calculated in the next section, this input is estimated to be 380 x 10^{10} g y^{-1}.

THE ATMOSPHERIC PHOSPHORUS CYCLE

I have made an estimate of the cycle of phosphorus in the atmosphere.

This cycle is presented in Fig. 8. My assumptions in the estimate are:

1. Total deposition of phosphorus over the continents is 321 x 10^{10}g y^{-1} and over the oceans is 135 x 10^{10} g y^{-1}.

2. Based on the estimate of Duce and Hoffman (1976) for vanadium, 10% of the anthropogenic emissions of phosphorus are deposited in the oceans.

3. Ten percent of the sea salt phosphorus is deposited on the continents (Ericksson, 1959, 1960; Blanchard, 1963).

4. The input of dust to the Atlantic Ocean from the Sahara Desert is 250 c 10^6 T y^{-1} (Lepple, 1975; Schütz, 1977). This dust contains 0.2% phosphorus (Lepple, personal communication).

5. The Sahara dust plume accounts for one third of the dust input to the oceans. The figure is completely arbitrary. However, it does not seem to be unreasonable. If I assume that the Sahara plume accounts for one third of the oceanic dust fall, 500 x 16^6 T y^{-1} come from other regions. This is in reasonable agreement with the estimate based on deep sea sediment accumulation rates (Goldberg as cited in Peterson and Junge, 1971).

6. The phosphorus content of the non-Sahara dust is 0.1%.

7. The input of phosphorus to the atmosphere from the oceans is the amount required to balance the oceanic portion of the cycle.

8. The input of phosphorus to the atmosphere on continental crustal material is the amount necessary to balance the cycle.

The cycle is presented in Table 12 and Fig. 8. Key comments are:

1. The larger fluxes in the cycle are given to three figures only to provide the esthetic pleasure of balancing the small fluxes. The fluxes should be treated as rough estimates probably good within a factor of 2 to 3.

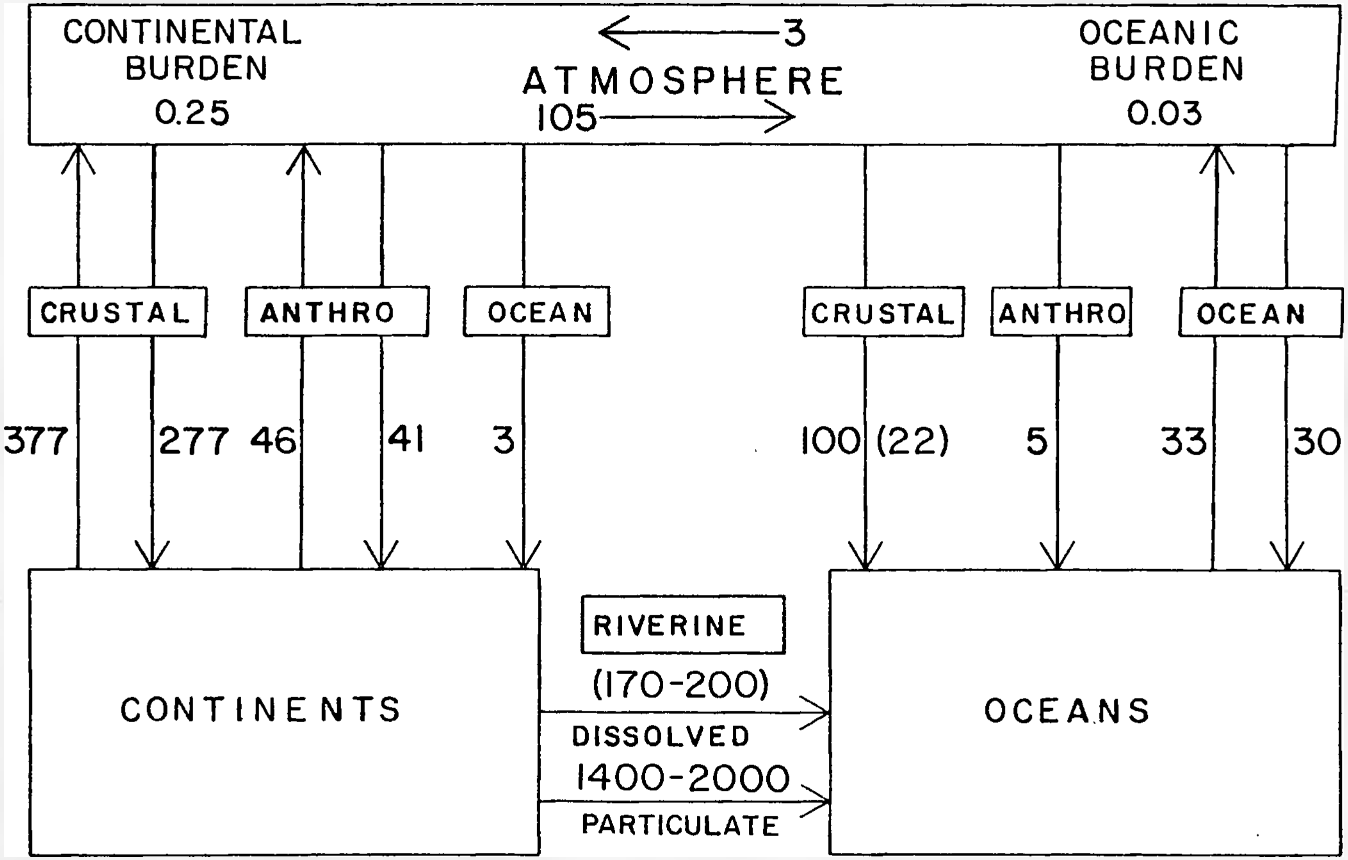
2. The phosphorus flux to the atmosphere on sea salt particles is estimated by difference to be 33 x 10^{10}g y^{-1}. This appears to be a

TABLE 12. FLUXES OF THE ATMOSPHERIC CYCLE OF PHOSPHORUS IN UNITS OF 10^{10} g y^{-1}

SOURCE	CONTINENTAL REGION			OCEANIC REGION		
	INPUT	DEPOSITION	TRANSFER	INPUT	DEPOSITION	TRANSFER
Crustal	377	277	-100	--	100	+100
Anthropogenic Emissions	46	41	-5	--	5	+5
Sea salt particles	--	3	+3	33	30	-3

Fig. 8 The atmospheric phosphorus cycle. The numbers in ( ) are the estimated inputs of sea water soluble phosphorus through rivers and through the atmosphere.

A PROPOSED PHOSPHORUS CYCLE



UNITS, 10^{10} g/yr

reasonable estimate when compared to the values of 10 x 10^{10}g y^{-1} and 100 x 10^{10}g y^{-1} calculated from the data of Eriksson (1959, 1960) and Blanchard (1963).

3. The phosphorus flux to the atmosphere on continental crustal material is ∿380 x 10^{10} g y^{-1} by difference. As previously noted, the values for phosphorus deposition onto the continents support the higher estimates of the input of crustal material of all particle sizes to the atmosphere.

4. Anthropogenic and oceanic inputs of phosphorus to the atmosphere are of the same order of magnitude and much less important on a global basis than the input of crustal material.

5. About 25% of the crustal phosphorus injected into the atmosphere is transported to the oceans. The Sahara dust plume alone accounts for about one half this value. Excluding the Sahara plume, about 15% of the total phosphorus deposition occurs over the oceans. This appears to be a reasonable number.

6. The input of industrially derived atmospheric phosphorus into the oceans is negligible on a global basis when compared to the input of phosphorus on crustal material. However, the input of industrial phosphorus emissions may be significant in areas such as the western North Atlantic adjacent to the highly industrialized east coast of North America (this thesis, Chap. 5).

7. Estimates of the riverine input of dissolved and particulate phosphorus range from 1400 x 10^{10}g y^{-1} (Emery et al., 1955) to 2000 x 10^{10}g y^{-1} (Lerman et al., 1975). The atmospheric pathway appears to account for between 5 and8% of the total phosphorus transport.

RESIDENCE TIME OF PHOSPHORUS IN THE ATMOSPHERE

Based on the atmospheric burdens of phosphorus and the estimated deposition rates, I calculate the residence times for continental and oceanic phosphorus to be 3 days and 1 day respectively. The residence time for phosphorus over the continents is in good agreement with the value of 3 days used by Robinson and Robbins (1971) in their estimation of the total global aerosol loading. However, the residence time calculated in this manner is only a gross average. Scale heights of particulates in the air over Europe vary from 1 to 3 Km (Junge, 1963) suggesting a wide range of particle sizes present in the atmosphere at various times. Small particle industrial emissions will have a residence time much longer than large particle crustal material, and will be transported much further before deposition.

The residence time for phosphorus over the ocean is much shorter, approximately 1 day. This figure may be low due to underestimation of the atmospheric burden of phosphorus over the oceans, as concentration data were not available for much of the world's oceans. However, this short residence time may also be real. About 30% of the Sahara dust plume is deposited in the nearest 325 Km to the African coast, suggesting very rapid fallout (Schütz et al., 1977). Robinson and Robbins (1971) suggest that the true residence time of sea salt particles may be significantly less than the 3 days used in their calculations. Junge (1963) points out that the typical 4-7 day residence time calculated for the tropospheric aerosol assumes a constant concentration throughout much of the troposphere. The profiles of Gillette and Blifford (1971) indicate that this assumption is not valid for sea salt, and the scale height of 0.9 Km estimated from their data is consistent with a very short aerosol residence time.

RELEASE OF PHOSPHORUS TO THE OCEANS

Much of the phosphorus deposited on the surface of the ocean is insoluble in sea water and not available as a plant nutrient. The exact fraction that will be released is difficult to determine, as it depends to a great extent on the rate of solubility of the phosphorus present, the susceptibility of the phosphorus to attack by microorganisms at the sea surface, and its residence time in the euphotic zone. An estimate of the easily available phosphorus can be obtained, however, by extracting samples of aerosol in low phosphorus sea water and measuring the amount of phosphorus released. Studies on Saharan aerosol and soil samples by Lepple (1975) indicate that ∿150 μg of phosphorus are released in sea water from a gram of dust. This is about 8% of the total phosphorus present. I have determined the phosphorus released on 37 samples of aerosol collected at Narragansett, Rhode Island and over the western North Atlantic. I find that 36% ± 15% of the total phosphorus is released in sea water. This is about 4 times the amount released by the desert aerosols. To estimate the global input of readily soluble phosphorus to the oceans, I assume that 8% of the phosphorus attributable to the Sahara aerosol is soluble, and 36% of the phosphorus from other regions is easily released. This amounts to 4×10^{10} and 18×10^{10} g of phosphorus respectively. Estimates of the current riverine input of dissolved phosphorus to the worlds oceans range from 170 to 200×10^{10} g y^{-1} (Stumm, 1973; Lerman, 1975; Emery et al., 1955; Pierrou, 1976). The atmosphere, then, appears to provide about 10% of the nutrient phosphate flux to the oceans.

CONCLUSIONS

The atmospheric phosphorus fluxes calculated in this paper are at best only first approximations of the true fluxes. The data which would enable more precise calculations to be made are simply not available for much of the globe. Analysis of the available data on phosphorus concentrations in and deposition rates from the global atmosphere suggest that:

1. An estimated 460 x 10^{10}g y^{-1} of phosphorus are deposited on the surface of the earth from the atmosphere. Of this amount 320 x 10^{10} g y^{-1} fall on the continents and 140 x 10^{10}g y^{-1} are estimated to fall onto the surface of the oceans.

2. The greater part of this fallout, 380 x 10^{10}g y^{-1}, is estimated to be of crustal origin. The contribution of the oceans to the atmospheric phosphorus flux is estimated to be 33 x 10^{10}g y^{-1}. Anthropogenic inputs are estimated to be 46 x 10^{10}g y^{-1}, the largest fraction of this input being on soil particles (∿20 x 10^{10}g y^{-1}) with the phosphate industry being the second largest source (15.4 x 10^{10}g y^{-1}).

3. The residence time of phosphorus in the atmosphere ranges from about one day over the oceans to about three days over the continents.

4. Studies on the release of atmospheric particulate phosphorus in sea water give release rates of ∿8% of the total phosphorus for aerosols derived from the Sahara desert and 36% for aerosols from the North American continent. From this data I estimate the atmospheric input of easily soluble phosphorus to the oceans to be 22 x 10^{10} g y^{-1}, or about 10% of the riverine input of dissolved phosphorus. The total phosphorus flux through the atmopsheric pathways appears to be between 5% and 8% of the flux of total particulate and dissolved phosphorus which is added annually to the oceans via rivers.

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CONCLUSIONS

Phosphorus in remote areas

The concentration of particulate phosphorus in the marine atmosphere in remote continental and marine areas is very low, a factor of 10^3 less than the concentration measured in urban areas. Concentrations of 200 pg m^{-3} were measured at the geographic South Pole; while in the remote Pacific concentrations of phosphorus in the marine atmosphere ranged from 20 to 800 pg m^{-3}. Particulate phosphorus in the marine air near Hawaii and Samoa comes from both continental and oceanic sources. The reactive phosphorus fraction is most closely associated with crustal material and its concentration at Hawaii is about twice the concentration measured on Samoa. An acid soluble inorganic fraction appears to have a marine source. The exact source could not be identified. The organic phosphorus fraction does not correlate with either aluminum or sodium. The material may be derived from more than one source. The deposition rate of phosphorus is estimated to be between 0.02 and 0.03 Kg $ha^{-1}y^{-1}$ in these island locations, about 10% of the rate of phosphorus deposition to the continents in the latitudes between 60°N and 60°S.

Phosphorus from the Sahara Desert

A major source of phosphorus input to the North Atlantic appears to be deposition of material from the Sahara dust plume. The estimated annual input of phosphorus to the North Atlantic between 15°N and 25°N is 50×10^{10} g y^{-1}. However, the greater part of this material is not readily soluble in sea water. Extraction studies of a limited number of samples by various investigators suggest that 100-200 ug of phosphorus are easily released in sea water from each gram of dust which falls on the ocean surface. Assuming a release of 135 ug g^{-1} of dust, a total of

3.3×10^{10} g of soluble phosphorus is added to this area of the North Atlantic annually. The rate of release of phosphorus deposited from the atmosphere to the sea surface needs to be determined on aerosol samples collected at a variety of locations in the North Atlantic in the path of the Sahara plume. The input of soluble phosphorus to the suface waters near the African coast is negligible when compared to the input from upwelling. However, further to the west, in the nutrient poor regions of the Sargasso Sea, aeolian deposition may provide nutrients to the surface waters at about the same rate as diffusion from nutrient rich deep waters.

Sources of particulate phosphorus over the western North Atlantic

Much of the phosphorus in the marine air over the western North Atlantic is of anthropogenic origin. A strong correlation is found between phosphorus and vanadium. Vanadium is an excellent indicator of the presence of combustion particulates in the atmosphere. The ratio of phosphorus to vanadium in the marine air of the western North Atlantic is 1.2:1; this value lies about half way between published values for fuel oil soot and coal fly ash. A highly significant correlation is found between phosphorus and vanadium not only in the reactive phosphorus fraction but also in the fraction which is normally considered to be organic. This indicates that much of the phosphorus in this nominally organic fraction was more likely a water insoluble inorganic form. The true amount of organic phosphorus can not be estimated from the data. Development of additional analytical methods for phosphorus is needed to enable the separation of organic and water insoluble inorganic fractions when large amounts of combustion particulates are present.

Phosphorus is also found to correlate significantly with aluminum and sea salt sodium, suggesting that phosphorus from crustal and marine sources is also present in the marine air of this region. The transport of crustal and anthropogenic phosphorus to the triangular area bounded by North America, a line along 65°W longitude and one along 25°N latitude is estimated to be between 5-10 x 10^9 g y^{-1}. Extraction studies on these filter samples indicate that about 35% of this phosphorus is easily released in sea water. Therefore, about 2-4 x 10^9g of soluble phosphorus are added to this geographic area annually. This appears to be about 10% of the riverine input of dissolved phosphorus to the same area.

Phosphorus on sea salt particles

Field studies in Narragansett Bay using the Bubble Interfacial Microlayer Sampler (BIMS) have shown that phosphorus is carried into the atmosphere on the drops from bursting bubbles and that it is enriched relative to sodium on these droplets. Enrichment appears to be a function of the phosphorus concentration in the surface water and of the wind velocity, but not of the depth at which bubbles are produced in the water. This suggests that the source of the phosphorus on the droplets is the sea surface microlayer. Enrichment of organic phosphorus in the BIMS samples was found to be a factor of ten higher than that of reactive phosphorus, indicating that the phosphorus stripped from the microlayer is predominately organic. No aluminum or vanadium could be detected on the filter samples. This suggests that little if any acid soluble inorganic phosphorus was present in the fraction considered organic.

Aerosol samples collected over the phosphorus rich waters of the Peru current were analyzed for reactive and organic phosphorus, along with sodium, aluminum, and vanadium. The greater part of the organic phosphorus fraction correlated with the sodium, indicating a marine source for this material. Calculated enrichment was in good agreement with those found for the BIMS study. The greater part of the reactive phosphorus correlated with aluminum, indicating a crustal source for this material. A small portion each of the reactive and organic fractions correlated with vanadium, incidating the presence of some combustion particulates in the samples also. While the "organic" fraction may contain more than truly organic phosphorus, the excess vanadium levels are low. The organic phosphorus which correlates with sodium is probably truly organic as would be expected from the BIMS study. It does appear that in nature phosphorus is injected into the atmosphere on sea salt particles.

The phosphorus cycle

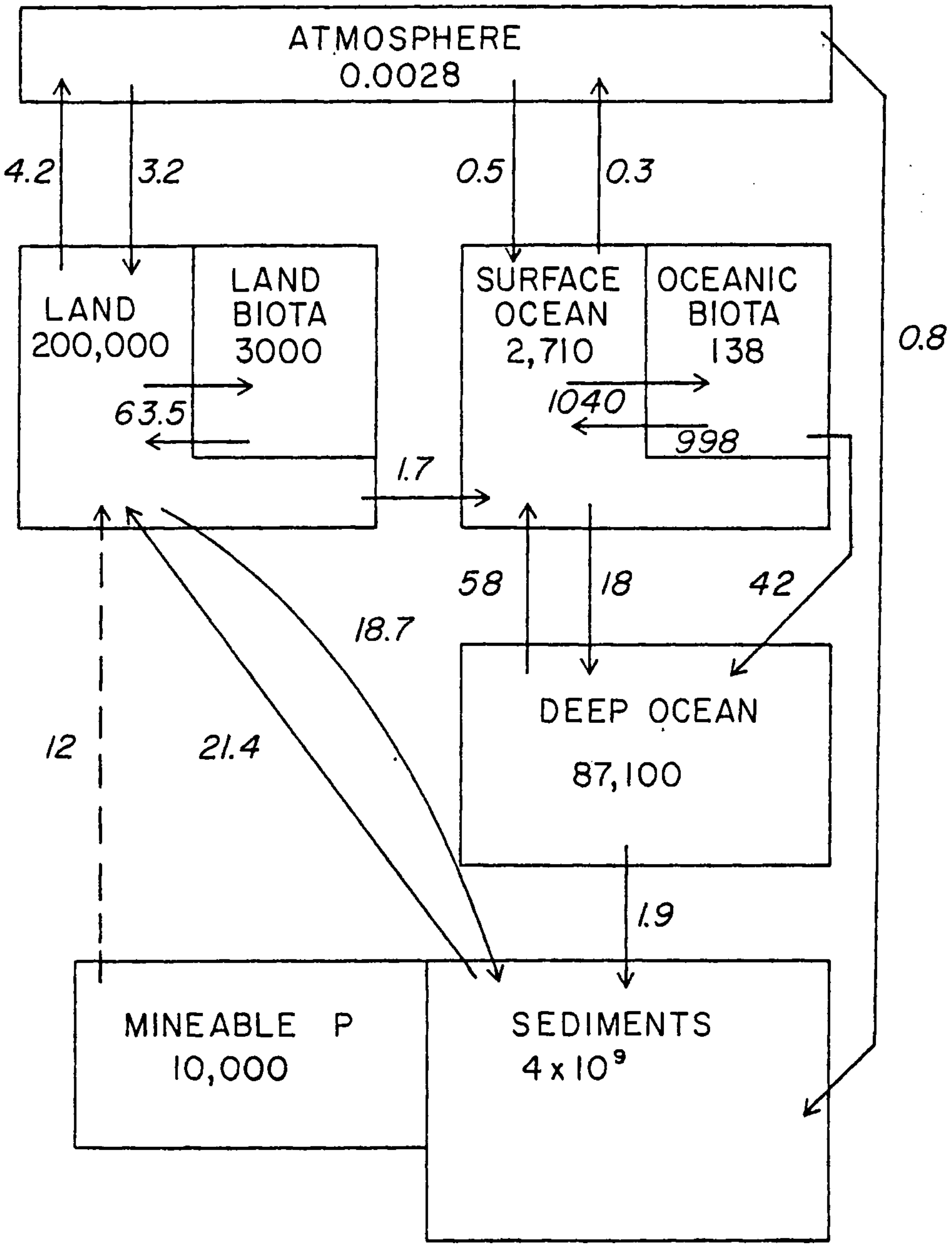
Using data developed in this study and published in the literature, fluxes in atmospheric portion of the phosphorus cycle has been estimated. These estimates must necessarily be very tentative, as data on the concentrations and deposition rates of phosphorus are missing for much of the worlds continents and oceans. The global cycle indicates that the major flux of phosphorus through the atmosphere is that of crustal phosphorus to the ocean. Inputs of anthropogenic phosphorus to the oceans and of marine phosphorus to the continents are much smaller globally, but may be important in local areas. A complete phosphorus cycle with an atmospheric portion has been synthesized in Fig. 1 by combining the atmospheric phosphorus cycle developed in this work with the cycle of Lerman (1975). Key points in this combined cycle are:

1. The atmosphere is by far the smallest reservoir in the cycle.
2. The flux of insoluble phosphorus to the sediments is about 5% of the particulate phosphorus delivered to the sediments

by rivers.

3. The estimated flux of soluble phosphorus to the ocean surface is about 30% of the riverine input of soluble phosphorus. However, about two thirds of this phosphorus is estimated to be recycled material present on sea salt particles. Thus the estimated net input of soluble phosphorus from the continents to the oceans is roughly 10% of the riverine input at the present time. It is possible that major climatic changes could change this ratio to an unknown degree.

Fig. 1 A complete phosphorus cycle obtained by combining the cycle of Lerman (1975) with the atmospheric cycle presented in Chap. 6. Reservoirs are in units of 10^{12}g, fluxes in units of 10^{12} g y^{-1}.


ATMOSPHERE
0.0028
4.2
3.2
0.5
0.3
LAND
200,000
LAND
BIOTA
3000
63.5
SURFACE
OCEAN
2,710
OCEANIC
BIOTA
138
1040
998
0.8
1.7
58
18
42
18.7
12
21.4
DEEP OCEAN
87,100
1.9
MINEABLE P
10,000
SEDIMENTS
4 x 10⁹

APPENDIX A

NOTES ON ANALYTICAL METHODS

PHOSPHORUS ANALYSIS

General

All phosphorus determinations were made using the well known molybdenum blue technique. The specific method used was the single solution ascorbic acid method of Murphy and Riley (1962). All measurements were made using one or ten centimeter cells in a Beckman D.U. spectrophotometer (wavelength of 885 mm, 0.2 slit width, red phototube).

Samples for total phosphorus were treated as follows: one quarter of a 20 x 25 cm Delbag 97/99 polystyrene filter was ashed in the presence of excess magnesium for 16 h at 550°C. After cooling of the ashed sample 1 ml of 1N HCl was added to the residue. After 30 min. the suspension was diluted with 5 ml doubly deionized (DD) water, and filtered through a 0.2 µm Nuclepore filter to remove insoluble material. The ashing beaker and filter were washed with two additional 5 ml aliquots of DD water. The filtrate was diluted to 40 ml and 4 ml of the mixed reagent of Murphy and Riley (1962) added. After a minimum of thirty minutes reaction time the color was measured spectrophotometrically.

A persulfate oxidation to oxidize organo-phosphorus compounds was performed be adding 40 ml of DD water and 5 ml of a 6.8% solution of potassium persulfate to one fourth of a filter in a 125 ml Erlenmeyer flask. The sample was autoclaved for 25 min at 125°C. The liquid was decanted and filtered through a 0.4 µm Nuclepore filter. Four ml of mixed reagent were added and the color was determined as above.

Reactive phosphorus was determined by extracting a quarter of a filter with 40 ml DD water and 100λ of 95% ethanol. The sample was agitated with a wrist action shaker for 30 min. The liquid was then decanted and filtered through a 0.4 μm Nuclepore filter. After addition of the mixed reagent, the color was determined as above.

Standards containing 1.24 μg and 12.4 μg P were prepared with reagent grade, dried KH_2PO_4 and run with each batch of samples. Separate standards were prepared to match the composition of the solutions derived from the ashing, persulfate oxidation, and water extraction techniques. All phosphate values from the persulfate oxidation and water extraction determinations were corrected for the amount of phosphorus lost due to rentention of some of the extracting or oxidizing solution in the filters.

Filter Blanks

Delbag Microsorban 97/99 polystyrene filter material was chosen as the matrix for the collection of atmospheric particulates in this study. The phosphorus content of the Delbag polystyrene filters was significantly less than the phosphorus content of either Whatman 41 cellulose or Gellman glass fiber filters (Table 1). Whatman 41 filters also appear to be much more variable in phosphorus content than the Delbag filters.

Prevention of phosphorus loss during high-temperature ashing

If pure (reagent grade) samples of inorganic and organic phosphorus compounds are ashed at high temperature (550°C) over a 16 hr period, over two thirds of the phosphorus initially present is lost, presumably through volitilization (Table 2). Following the suggestion of Dunlop (1960) each filter sample was soaked in 20 ml of a 25 ppm solution of magnesium nitrate (Fischer Atomic Adsorbtion Standard diluted 40/1). Two drops of ethyl alcohol were added as a wetting agent. The filter

TABLE 1. PHOSPHORUS CONTENT OF VARIOUS FILTER MATERIALS

FILTER MATERIAL	PHOSPHORUS CONTENT ng cm^{-2} PERSULFATE OXIDATION[1]	PHOSPHORUS CONTENT ng cm^{-2} HIGH TEMPERATURE ASHING (550°C)
Delbag (polystyrene)	Not detectable (4)	2.86 ± 0.59 (28)
Whatman 41 (cellulosic)	2.56 ± 0.52 (4)	9.41 ± 4.56 (11)
Gellman (glass fiber)	8.52 ± 0.64 (4)	Not determined

[1] Method of Menzel and Corwin (1965).

( )number of samples analyzed

TABLE 2. THE EFFECT OF MAGNESIUM ON THE LOSS OF PHOSPHORUS DURING HIGH TEMPERATURE ASHING

COMPOUND	Amount Added ng l^{-1}	No Magnesium Added		Magnesium Added	
		Amount Recovered ng l^{-1}	% Recovered	Amount Recovered ng l^{-1}	% Recovered
KH_2PO_4	40	12.8 ± 1.8	32.1 ± 4.4	42.4 ± 0.3	106 ± 0.8
Lecithin	40[1]	13.1 ± 0.6	33.0 ± 3.1	36.0 ± 0.7	90.0 ± 3.6
B - Glycero-Phosphoric acid	40[2]	11.1 ± 1.1	27.7 ± 5.4	46.7 ± 0.2	116.7 ± 1.2
Fructose 1-6 diphosphate	80	14.8 ± 5.2	18.6 ± 6.5	59.6 ± 0.7	74.6 ± 1.7

[1] Molecular weight uncertain

[2] Purity uncertain

was then dried overnight at 90-95°C. Following this treatment, the filters were ashed at 550°C for 16 hrs. With the exception of the fructose 1-6 diphosphate, recoveries were better than 90% of the nominal amount added. The reasons for the low recovery of the fructose 1-6 diphosphate are not known, since a somewhat similar compound, inosital hexaphosphate, shows complete recovery after ashing at 550°C in the presence of magnesium (Table 4).

Low temperature ashing

An alternative approach to the prevention of phosphorus loss during ashing is to ash the filters in a commercial low temperature asher such as the LFE Corporation unit which uses molecular oxygen excited by a radio frequency generated electromagnetic field to ash the samples. Unfortunately, Delbag filters do not ash in these devices, evidently due to the formation of an impermiable outer layer at the onset of ashing which prevents the penetration of molecular oxygen into the filter matrix.

Recovery of inorganic phosphates after high-temperature ashing

Samples of three commercially available inorganic phosphates were treated with excess magnesium, and ashed at 550°C in a manner identical to the procedure used with the filter samples. The phosphate compounds were aluminum phosphate ($AlPO_4$), iron phosphate ($FePO_4 \cdot xH_2O$), and calcium phosphate $Ca_{10}(OH)_2(PO_4)_6$. After ashing, the samples were digested with 1 ml 1 N HCl diluted to 5 ml with DD water, and filtered through 0.2 µm Nuclepore filters. Dissolution of the calcium phosphate samples were complete while significant amounts of undissolved material remained in the samples of aluminum and iron phosphates. The recoveries of phosphorus for these three materials are given in Table 3. Complete recovery of phosphorus was obtained with the calcium and iron phosphates. Less than 50% of the aluminum phosphate was recovered in this method. Since the iron phosphate was of indeterminate molecular weight, the percentage recovery of the sample was calculated based on the phosphorus content determined on samples completely dissolved in concentrated HCl. Recoveries of phosphorus from the aluminum and calcium phosphate samples are based on the assumption that these materials have a purity of 100%.

A considerable amount of red acid-insoluble particulate matter is present in the iron phosphate samples after ashing at 550°C. However, complete recovery of the phosphorus present occurs. These observations suggest that an interaction occurs between the iron phosphate and excess magnesium present. The phosphorus is converted to magnesium phosphate while the iron is then oxidized to iron oxides. A similar process may occur to some extent during the ashing of aluminum phosphates, as recovery of phosphorus after ashing is about twice as high as the recovery obtained by digestion with concentrated HCl (46% vs 26%).

Calcium phosphates of the apatite family represent by far the major amount of phosphorus on the crust of the earth (Van Wazer, 1958). The concentrations of the other mineral phosphates are negligible compared to that of the apatites. The low recovery of aluminum phosphates in this method, then, is not believed to have introduced any significant error into the results.

High temperature ashing vs persulfate oxidation-organics

Table 4 presents the results of a brief study comparing the recoveries of phosphorus obtained by ashing samples of organic phosphorus

TABLE 3. RECOVERY OF INORGANIC PHOSPHATES IN THE TOTAL PHOSPHORUS METHOD

COMPOUND	P ADDED µg	P RECOVERED µg	% RECOVERY
$AlPO_4$	550	220	40
	430	230	53
	350	110	31
	750	440	59
			46 ± 13
$FePO_4 \cdot XH_2O$	230[1]	220	96
	200[1]	230	115
	250[1]	260	96
	190[1]	180	95
			101 ± 10
$Ca_{10}(OH)_2(PO_4)_6$	390	400	103
(approximately)	280	290	104
	190	200	105
	150	150	100
			103 ± 2

[1] Assumes 12.7% phosphorus based on complete dissolution of material in concentrated HCl.

TABLE 4. A COMPARISON OF THE HIGH TEMPERATURE ASHING AND PERSULFATE OXIDATION TECHNIQUES FOR ORGANIC PHOSPHORUS ANALYSIS

MATERIAL	Nominal Amount Added µg l^{-1}	Amount Recovered 550°C Ashing µg l^{-1}	Amount Recovered Persulfate Oxidation µg l^{-1}	Ratio $\frac{\text{Persulfate}}{\text{Hi-Temperature}}$
Lecithin	40[1]	36.0 ± 0.07	35.2 ± 2.4	0.98
B-Glycero-Phosphoric acid	40[2]	46.7 ± 0.2	41.1 ± 1.4	0.89
Adenosine -5'-monophosphate	40[2]	42.0 ± 0.7	36.0 ± 0.4	0.86
Fructose 1-6 diphosphate	80[2]	59.6 ± 0.7	50.1 ± 2.2	0.84
Inositol hexaphosphate	930[2]	1030 ± 100	105 ± 11	0.10

[1] Molecular weight uncertain

[2] Assumes 100% purity

compounds at 550°C in the presence of excess magnesium with those obtained by the persulfate oxidation technique of Menzel and Corwin (1965). For most organic phosphates tested, the recovery of phosphorus using the persulfate oxidation method is between 85-100% of the recovery obtained with the ashing technique. Sugar phosphates appear to be much more resistant to oxidation by persulfate. Phosphorus recovery during persulfate oxidation of inositol hexaphosphate material amounts to only 10% of the recovery obtained when the sample is ashed at 550°C.

Recovery of phosphorus from Delbag filters

High-temperature ashing

Table 5 shows that an average of 95% of the phosphorus added to 5 x 6 cm Delbag filter samples is recovered when the filters are ashed at 550°C in the presence of excess magnesium.

Persulfate oxidation

Two sequential persulfate oxidations were made on a series of Delbag filter samples collected at Narragansett, R.I. and over the North Atlantic. The purpose of the study was to determine if additional phosphorus was released during a second oxidation step, or if one oxidation was sufficient for the release of all persulfate oxidizable phosphorus. After correction for the phosphorus-containing solution which is retained in the filter after the first oxidation, individual samples had a first oxidation recovery varying between 87 and 106% of the phosphorus released in two oxidations (Table 6). The average recovery was 97%, with a standard deviation of the mean of 1%. The results of this study indicate that the error introduced by doing only one persulfate oxidation of the filter samples was small. Only one oxidation was performed on the samples

TABLE 5. PHOSPHORUS RECOVERY - ASHED DELBAG FILTERS 550°C FOR 16 HOURS

P ADDED µg	P MEASURED µg	NET P µg	% RECOVERY
Blank Filter	1.03 ± 0.08	-	-
1.24 µg	2.18 ± 0.02	1.15 ± 0.08	92.7
2.48 µg	3.43 ± 0.07	2.40 ± 0.11	96.7
4.96 µg	5.80 ± 0.20	4.77 ± 0.22	96.1

TABLE 6. RELEASE OF PHOSPHORUS IN SEQUENTIAL PERSULFATE OXIDATIONS

SAMPLE	TOTAL P RELEASED ONE OXIDATION µg	TOTAL P RELEASED TWO OXIDATIONS µg	P 1 OXID. / P 2 OXID.
1	4.26	4.30	0.99
2	2.94	2.88	1.02
3	0.16	0.16	1.00
4	5.83	5.77	1.01
5	8.85	0.04	0.98
6	3.01	3.07	0.98
7	2.88	3.02	0.95
8	5.40	5.48	0.99
9	2.09	2.12	0.99
10	2.66	2.78	0.96
11	0.33	0.31	1.06
12	4.54	4.60	0.99
13	5.92	6.08	0.97
14	6.24	6.29	0.99
15	2.72	2.86	0.95
16	0.20	0.20	1.00
17	2.56	2.51	1.01
18	1.20	1.22	0.98
19	3.59	3.69	0.97
20	4.87	4.97	0.98
21	0.29	0.27	1.07
22	2.06	2.06	1.00
23	6.05	6.27	0.96
24	1.54	1.71	0.88
25	6.05	6.42	0.94
26	0.27	0.31	0.87
27	1.72	1.70	1.02
28	2.93	2.87	1.02
29	2.83	3.06	0.92
30	0.99	0.99	1.00

TABLE 6. RELEASE OF PHOSPHORUS IN SEQUENTIAL PERSULFATE OXIDATIONS (continued)

SAMPLE	TOTAL P RELEASED ONE OXIDATION µg	TOTAL P RELEASED TWO OXIDATIONS µg	$\frac{\text{P 1 OXID.}}{\text{P 2 OXID.}}$
31	1.05	1.10	0.95
32	16.6	17.7	0.94
33	8.30	9.00	0.92
34	4.04	4.16	0.97
35	4.88	5.12	0.94

Mean and σ of mean = 0.97 ± 0.1

reported in this study, and no correction factor was applied.

Reactive phosphorus

Filter quarters were spotted with 0.25, 0.50, and 1.00 μg of phosphorus as KH_2PO_4, then extracted with 40 ml DD water for 30 minutes with agitation. A small amount (100 λ) of 95% ethanol was added as a wetting agent. All values were corrected for water retained in the filter matrix. Recoveries on the first test appeared to be low (<90%) at the 0.5 and 1.0 μg phosphorus levels (Table 7). Two additional checks using filters containing 1.24 μg P showed essentially complete recovery (Table 7). No additional corrections therefore were applied to the reactive phosphorus values obtained on the field samples.

Summary

Based on the experiments and tests discussed above, phosphorus levels in samples of atmospheric particulate matter were determined as follows:

1. Delbag filters were used to collect the samples.

2. Total phosphorus was determined by ashing filter samples at 550°C in the presence of excess magnesium to prevent loss of volitile phosphorus compounds. Following dilution, phosphorus was determined colorimetrically using the method of Murphy and Riley (1962).

3. Persulfate releasable phosphorus was determined by oxidizing filter samples with a potassium persulfate solution per the method of Menzel and Corwin (1965). Following oxidation and filtration, phosphorus was determined colorimetrically. All results were corrected for solution loss during filtration.

4. Reactive phosphorus was determined by agitating filter samples

TABLE 7. RECOVERY OF REACTIVE PHOSPHORUS FROM DELBAG FILTERS

AMOUNT ADDED µg	AMOUNT RECOVERED µg	% RECOVERY
0.25	0.26 ± 0.04	103 ± 15
0.50	0.44 ± 0.06	88 ± 12
1.0	0.89 ± 0.06	89 ± 3
1.24	1.21 ± 0.09	98 ± 2
1.24	1.29 ± 0.01	104 ± 1

in doubly distilled water for 30 min, followed by filtration. Phosphorus in the filtrate was determined colorimetrically. All results were corrected for solution loss during filtration.

SODIUM, ALUMINUM, AND VANADIUM ANALYSES

General

Neutron activation analysis was used to determine the amounts of sodium, aluminum and vanadium contents of the atmospheric particulate matter collected on Delbag filters. The irradiations were done using the swimming pool reactor facility of the Rhode Island Nuclear Science Center at Narragansett, Rhode Island. This reactor can generate thermal neutron fluxes of up to 4×10^{12} n $cm^{-2}s^{-1}$.

Because of short half-lives of aluminum (2.31 min) and vanadium (3.76 min) and the presence in most of the filters of large quantities of sea salt, short irradiations were used (30 sec) and the samples were counted as quickly as possible after completion of the irradiation. Longer irradiation times proved to be unworkable due to the high levels of background activity from the sodium and chlorine present in the salt particles. Only by using very short irradiations to minimize sodium and chlorine activity and by counting the samples very quickly after irradiation could the aluminum and vanadium gamma ray peaks be seen. Even with this approach, vanadium was not detectable in the samples from American Samoa. The specific procedure used was as follows:

Sample preparation

One quarter of a filter sample was pressed in a teflon lined, stainless steel pellet press under ~600 N force to form a cyclindrical pellet about 2.0 cm diameter and 2.0 cm in length. The pellet was then sealed in a small polyethylene bag and placed in a 7 dram polyethylene vial for irradiation. All filter quartering and pelleting operations took place in a liminar flow clean bench.

Standards were prepared by spotting blank Delbag filter quarters with appropriate quantities of standard solutions. Fisher brand atomic adsorption standards were used for aluminum and vanadium. To match as closely as possible the matrix of the actual field samples, Copenhagen water of 19.275‰ chlorinity was used to provide the sodium standards. No aluminum or vanadium could be detected in pure sodium standards made using this water. After drying in the clean bench the filters were pelleted and sealed in the same manner as the samples.

As a flux monitor, 2 μg of Fisher brand manganese AA standard were spotted on W-41 filter paper, dried, and placed in the bottom of the 7 dram vial before the sealed sample was added.

Irradiation and counting

The vial to be irradiated was placed in a polyethylene rabbit which was then transported pneumatically to the reactor core. Following return of the sample, the pellet was transferred as rapidly as possible to a clean, acid-washed 250 ml plastic beaker and counted for 400 s clock time on a 20 cc Ge(Li) detector (resolution of 2.3 KeV for the 1,332 KeV gamma ray of ^{60}Co) coupled to a Nuclear Data 2200 4096 channel analyzer with a computer compatible magnetic tape output (Ampex TM-7). Counting began between 105 and 135 seconds after the beginning of a 30-second irradiation. Constant geometry was maintained for all samples. Immediately after the finish of the sample count, the vial containing the manganese flux monitor was counted for 200 seconds.

Spectra processing

A computer program of Dr. J.L. Fasching of the University of Rhode

Island Chemistry Department was used to process the Ge(Li) spectra acquired.

Dead time corrections

In situations such as the counting of a pure short-lived radionuclide or of a short-lived radionuclide in the presence of one or more long-lived radioactivities, exact solutions have been developed to enable one to obtain the true counts of the isotope from the observed counts and the average dead time of the detector (DeSoete et al., 1972). However with a mixture of isotopes of varying half-lives, most corrections require a knowledge of the dead time as a function of clock time during counting (Schonfeld, 1966; Gavron, 1969). These data are not obtainable with the unit that was used in this work. Consequently I have expanded a technique provided me by Dr. M.L. Bender of the University of Rhode Island Graduate School of Oceanography to arrive at an approximation method for dead time corrections.

Let;
$$DT = C_1 \exp(-\lambda_1 t) + C_2 \exp(-\lambda_2 t) + \ldots, + C_i \exp(\lambda_i t) + C_j \exp(-\lambda_j t) \qquad (1)$$

where:

DT = instantaneous dead time at time t

C_i = the fraction of the total dead time contributed by element i at time t

λ_i = the decay constant for element i

and, for radionuclide i:

$$R'_i = A_i \int_{t_o}^{t_f} \exp(-\lambda_i t) \cdot [1-DT]dt \qquad (2)$$

where:

R'_i = observed counts of nuclide i over the counting period

A_i = empirical coefficient

substituting (1) into (2) and integrating:

$$R'_i = A_i \frac{\exp(-\lambda_i t_f) - \exp(-\lambda_i t_o)}{\lambda_i} + \qquad (3)$$

$$C_1 \frac{\exp[(-\lambda_i + \lambda_1)\ t_f] - \exp[(\lambda_i + \lambda_1)\quad t_o]}{\lambda_i + \lambda_1} +$$

$$C_2 \frac{\exp[(\lambda_i + \lambda_2)\ t_f] - \exp[(\lambda_i + \lambda_2)\ t_o]}{\lambda_i + \lambda_2} +$$

$$\ldots + C_i \frac{\exp(2\ \lambda_i t_f) - \exp(2\ \lambda_i t_o)}{2\lambda_i} +$$

$$C_j \frac{\exp[(\lambda_i + \lambda_j)\ t_f)] - \exp[\ (\lambda_i + \lambda_j)]\ t_o}{\lambda_i + \lambda_j}$$

$$= A_i K_i \qquad (4)$$

The actual counts (R) are equal to:

$$R_i = A_i \int_{t_o}^{t_f} \exp(-\ \lambda_i t)\ \ dt \qquad (5)$$

$$= A_i \frac{\exp\ (-\lambda_i t_o) - \exp\ (-\lambda_i t_f)}{\lambda_i}$$

$$= A_i J_i \qquad (6)$$

Solving (4) for A_i and substituting into (6) yields

$$R = R'\ (J_i\ /\ K_i) \qquad (7)$$

If the instantaneous dead time is known as a function of clock time, the coefficients C_1, C_2 ....C_j can be evaluated directly. These data however are not available in this work. The following approximation has been used instead:

$$\text{Let } C_i = k \frac{R'_i}{\sum_{i=1}^{j} R'} = fg_i \qquad (8)$$

The proportionality constant f is evaluated by substituting into equation (1)

$$DT = f\,[g_1 \exp(-\lambda_1 t)\; g_2 \exp(-\lambda_2 t) + \ldots\ldots + g_i \exp(-\lambda_i t) + g_j \exp(-\lambda_j t)] \qquad (9)$$

and setting DT equal to the average dead time as measured by pulsar counts during the counting period. t is set equal to $t_0 + \frac{t_0 + t_f}{2}$. The assumption here is that the instantaneous dead time is equal to the average dead time half way through the count. Once f has been estimated, the individual C_i's can be calculated, and equation (3), (5) and (7) evaluated. The calculations are tedious and have been programmed in Fortran as shown in Appendix B. The program will calculate corrected counts for sodium, aluminum, and vanadium. Inputs include the raw counts of these three elements plus raw counts of chlorine, manganese, magnesium, and bromine. These elements account for over 90% of the counts in a typical sample of marine atmospheric particulates.

Half-life and flux corrections

The counts obtained from all samples, standards, and flux monitors were corrected for decay during the time interval between the times of irradiation and counting. Using the flux monitors, all samples and standards were counted to a common flux equivalent of 5000 manganese counts. Both the decay and flux correction calculations were incorporated into the computer program given in Appendix B.

Adequacy of corrections

In Figs. 1, 2, and 3, plots are shown of corrected counts as a function of the amount of the element present in the standard. The corrections appear to do a reasonably good job of providing a linear correlation between counts and amount of material present.. The intercepts of the sodium and vanadium regression lives are not significantly different from zero; this is consistent with irradiations of blank Delbag filters which do not show sodium or vanadium to be present. The presence of aluminum in Delbag filter blanks is reflected in the non-zero intercept of this regression line.

Fig. 1 Corrected sodium counts vs weight of sodium in standards.

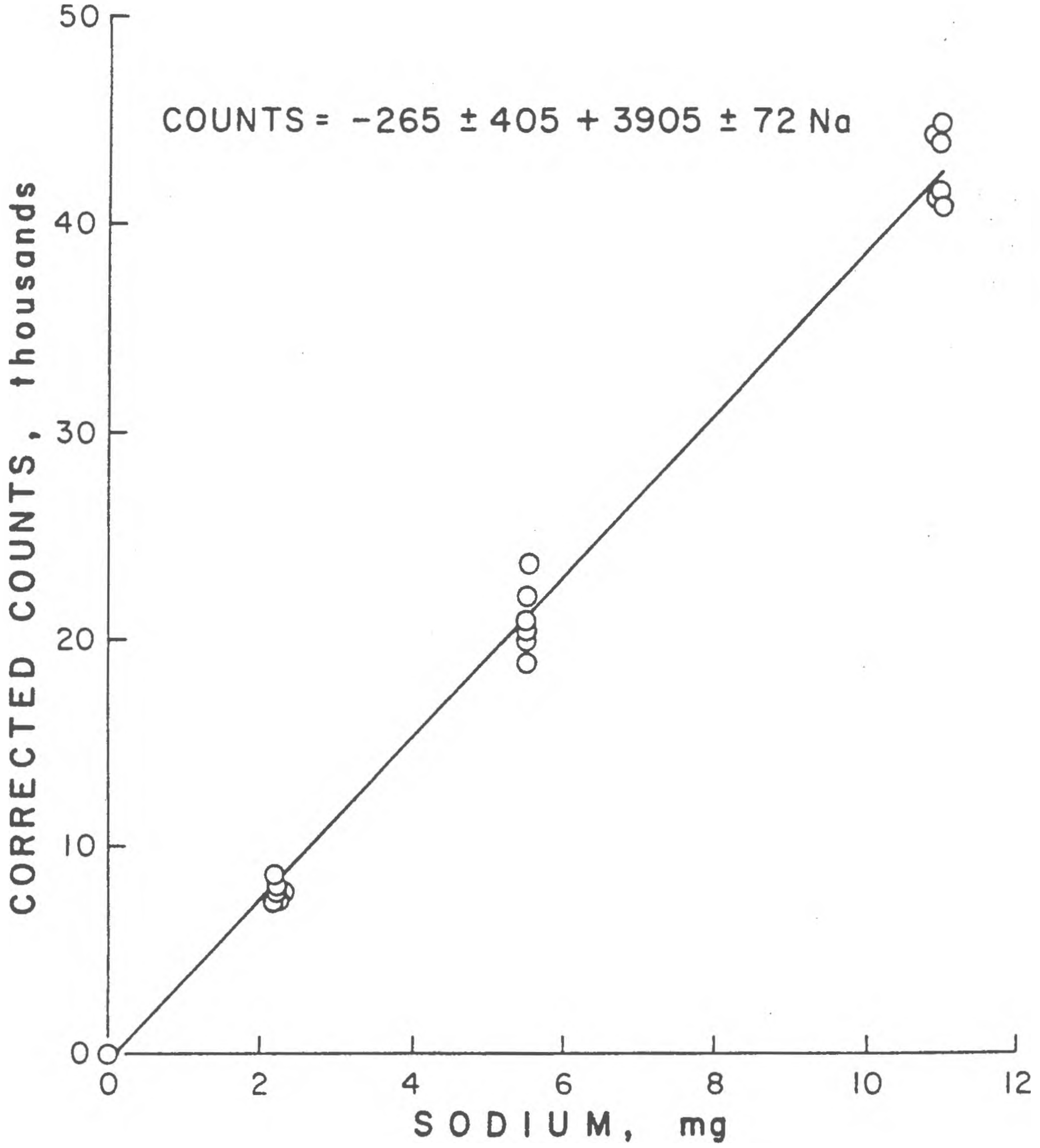

COUNTS = −265 ± 405 + 3905 ± 72 Na
CORRECTED COUNTS, thousands
0
10
20
30
40
50
SODIUM, mg
0
2
4
6
8
10
12

Fig. 2 Corrected aluminum counts vs. weight of aluminum in standards.

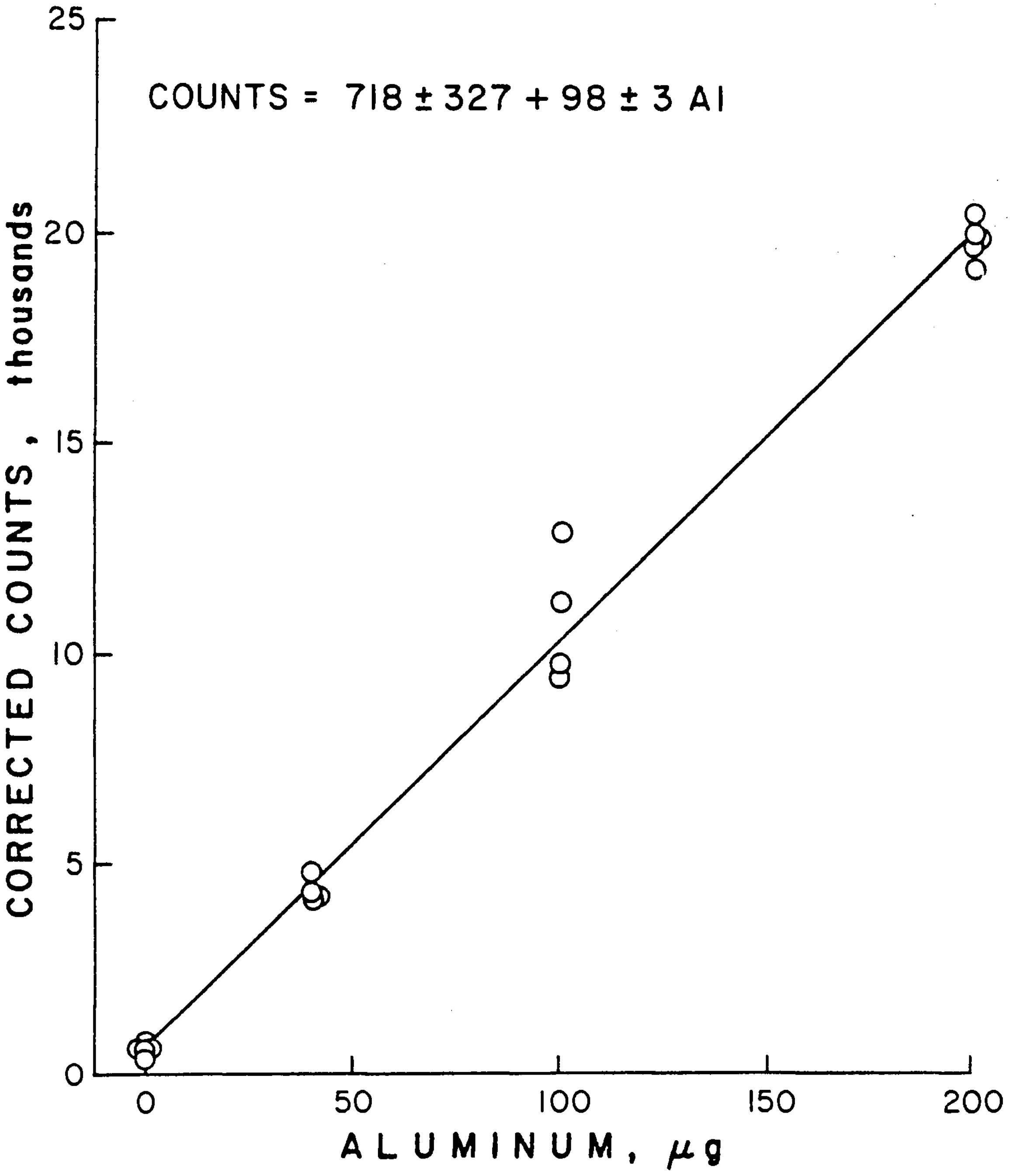
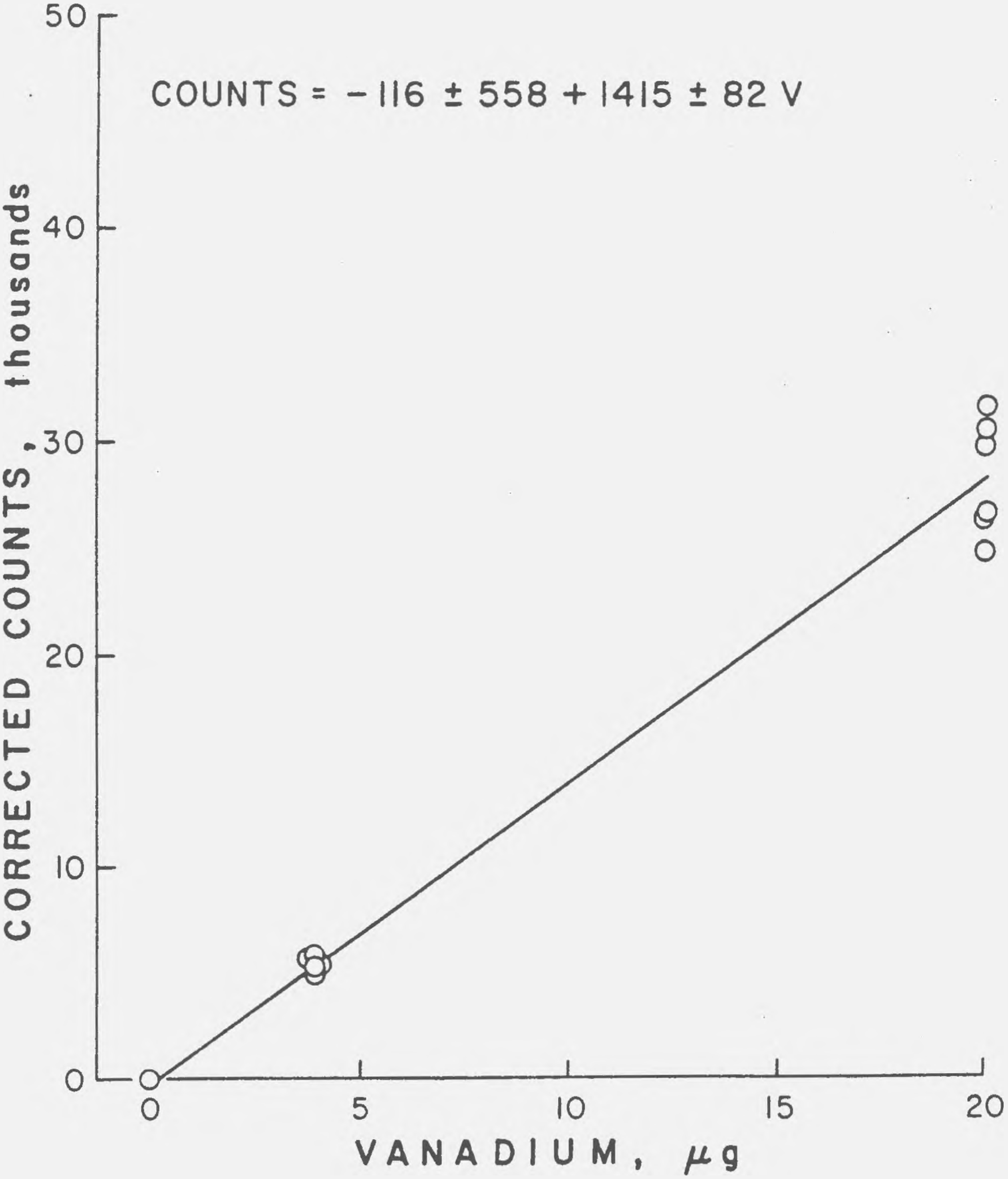

COUNTS = 718 ± 327 + 98 ± 3 Al
CORRECTED COUNTS , thousands
25
20
15
10
5
0
0
50
100
150
200
ALUMINUM, μg

Fig. 3 Corrected vanadium counts vs weight of vanadium in standards.


COUNTS = − 116 ± 558 + 1415 ± 82 V
CORRECTED COUNTS, thousands
50
40
30
20
10
0
0
5
10
15
20
VANADIUM, μg

APPENDIX B

FORTRAN PROGRAM FOR DEAD TIME, HALF LIFE, AND FLUX CORRECTIONS

```
C PROGRAM WRITTEN BY W.F. GRAHAM TO CORRECT GAMMA RAY COUNTS OF UP TO
C SIX   ELEMENTS FOR DEAD TIME AND FLUX VARIATIONS
C FIRST VERSION, JULY 1976
      REAL METAL(6),LAMBDA(7)
      INTEGER SAMPLE,TAGWD
      DIMENSION              HLFLV(7),ELMNT(7),PARTCO(7),APART(7),
     1CORCNT(6), FINCNT(6), TOP(6),BOT(6),HICNT(6),
     1SNAME(3),GROUP(3),ELNAME(7,3)
C
C READ IN DATA FOR SAMPLE GROUP. SAMPLE = NO OF SAMPLES, NUMET IS THE
C NUMBER OF ELEMENTS ON WHICH CORRECT COUNTS ARE DESIRED, NUMELM IS THE
C NUMBER OF ELEMENTS IN THE DEAD TIME CORRECTION, CNTYM = COUNT TIME,
C STDFLX = STANDARD FLUX TO BE USED IN CORRECTIONS,
C HLFLV = THE HALFLIVES OF THE ELEMENT IN SECONDS
C
   10 READ (5,12)SAMPLE, NUMET, NUMELM, CNTYM, STDFLX,STDDEC,
     1(GROUP(I),I=1,3)
   12 FORMAT(3I2,4X,F5.0,2F10.0,5X,3A4)
      IF(SAMPLE.LT.1) GO TO 999
      DO 15 I=1,NUMELM
      READ(5,14)(ELNAME(I,J),J=1,3),HLFLV(I)
   14 FORMAT (3A4,8X,F10.0)
      LAMBDA(I) = 0.693/ HLFLV(I)
   15 CONTINUE
C
C WRITE OUT SAMPLE BATCH INPUT DATA
C
   19 FORMAT (' ',7X,I2,5X,3A4,I3,9X,I2,6X,F5.0,4X,F6.0)
      WRITE(6,22)
   22 FORMAT ('1',1X,'SAMPLE BATCH INFORMATION'//6X'NO. OF',5X,'GROUP',
     13X,'NO. OF',5X,'NO. OF',5X,'COUNT',3X,'STANDARD'/6X,'SAMPLES',12X,
     1'UNKNOWNS',3X,'ELEMENTS',3X,'TIME',5X,'FLUX')
      WRITE(6,19) SAMPLE,(GROUP(I),I=1,3),NUMET,NUMELM,CNTYM,STDFLX
      WRITE(6,27)
   27 FORMAT('0',12X,'ELEMENT',8X,'HALFLIFE',13X,'LAMBDA')
      DO 24 L = 1,NUMELM
      WRITE (6,23)(ELNAME(L,K),K=1,3),HLFLV(L),LAMBDA(L)
   23 FORMAT (' ',10X,3A4,F11.0,E22.6)
   24 CONTINUE
C
C READ IN DATA FOR INDIVIDUAL SAMPLES. SNAME=SAMPLE NAME, TAGWD=TAGWORD,
C DECYTM =DECAY TIME OF SAMPLE, PULSAR = PULSAR COUNTS OF SAMPLE.
C METAL= COUNTS OF ELEMENT AT GAMMA RAY ENERGY OF INTEREST. ELMNT =TOTAL
C COUNTS OF ELEMENT OVER ALL GAMMAS. FLXTYM, FLUX, AND FLXPUL   ARE THE
C DECAY TIME, FLUX COUNTS, AND FLUX PULSAR RESPECTIVELY OF THE FLUX
C MONITOR. DECYTM IS IN SECONDS. FLXTYM IN MINUTES. FLXCT= FLUX COUNT
C TIME IS SECONDS
C
```

```
      E1 = -LAMBDA(JC) * DECTYM
      E2 = -LAMBDA(JC) * FINTYM
      C1 = EXP(E1)
      C2 = EXP(E2)
      BOT(JC) = C1 - C2
      ELFAC = (C1-C2)/LAMBDA(JC)
      FACT = FACT + ELFAC
      DO 80 KD = 1,NUMELM
      TOTLAM = LAMBDA(JC) + LAMBDA(KD)
      D1 = -TOTLAM * FINTYM
      D2 = -TOTLAM * DECTYM
      F1 = EXP(D1)
      F2 = EXP(D2)
      HHISFA = (F1-F2)/TOTLAM
      THISFA=HHISFA*PARTCO(KD)
      FACT = FACT + THISFA
   80 CONTINUE
      CORFAC = METAL(JC)/FACT
      CORCNT(JC) = CORFAC * ELFAC
  100 CONTINUE
C
C     CORRECT SAMPLES FOR DIFFERENCES IN DECAY TIME
C
      TIMFIN = STDDEC + CNTYM
      DO 18 NN=1,NUMET
      A1 = -LAMBDA(NN)*STDDEC
      A2 = -LAMBDA(NN)*TIMFIN
      TOP(NN) = EXP(A1) - EXP(A2)
   18 CONTINUE
      WRITE(6,114)
  114 FORMAT('0',8X,'ELEMENT',4X,'DECAY CORRECTION')
      DO 120 MM=1,NUMET
      FUDGE = TOP(MM)/BOT(MM)
      HICNT(MM) = FUDGE * CORCNT(MM)
      WRITE(6,115)(ELNAME(MM,MN),MN=1,3),FUDGE
  115 FORMAT('0',6X,3A4,5X,F5.3)
  120 CONTINUE
C
C CALCULATE THE FLUX CORRECTION FOR THIS SAMPLE. FIRST, CORRECT THE
C FLUX FOR DECAY.
C
      Q =  0.0044742 * FLXTYM
      AFLUX = FLUX * EXP(Q)
      CORFLX = AFLUX * (FLXCT * 60.0)/FLXPUL
      FLXCOR = STDFLX / CORFLX
      WRITE (6,148) AFLUX, CORFLX, FLXCOR
  148 FORMAT ('0',6X,2F12.0,6X,F6.3)
      DO 150 JD = 1,NUMET
```

```
      DO 750 I = 1,SAMPLE
      READ (5,25)(SNAME(J),J=1,3),TAGWD,DECTYM,PULSAR
   25 FORMAT (3A4,8X,I10,2F10.0)
      READ (5,30)(METAL(J),J=1,NUMET)
   30 FORMAT (7F10.0)
      READ (5,30)(ELMNT(K),K=1,NUMELM)
      READ (5,35) FLXTYM, FLUX, FLXPUL,FLXCT
   35 FORMAT (F10.2,3F10.0)
C
C WRITE OUT RESULTS AND SAMPLE INPUT DATA
C
      WRITE(6,200)
  200 FORMAT ('1',2X,'SAMPLE INPUT INFORMATION')
      WRITE(6,220)
  220 FORMAT ('0',6X,'SAMPLE CODE',4X,'TAGWORD',5X,'DECAY TIME',7X,
     1'PULSAR')
      WRITE(6,230)(SNAME(M),M=1,3),TAGWD,DECTYM,PULSAR
  230 FORMAT ('0',8X,3A4,I6,7X,F6.0,6X,F10.0)
      WRITE(6,240)(METAL(J),J=1,NUMET)
      WRITE(6,240)(ELMNT(J),J=1,NUMELM)
  240 FORMAT ('0',7F10.0)
C
C CALCULATION OF THE INDIVIDUAL COEFFICIENTS TO BE USED FOR THE
C DEAD TIME CORRECTION.
C
      AVTYM = DECTYM + CNTYM/2.0
      FINTYM = DECTYM + CNTYM
      DPART = 0.0
      TOTCNT = 0.0
      DO 55 JACK = 1,NUMELM
      TOTCNT = ELMNT(JACK) + TOTCNT
   55 CONTINUE
      DO 60 JA = 1,NUMELM
      PARTCO(JA) = ELMNT(JA)/TOTCNT
      POWER = -LAMBDA(JA)*AVTYM
      APART(JA) = PARTCO(JA)* EXP(POWER)
      DPART = DPART + APART(JA)
   60 CONTINUE
      DT = (1 - PULSAR/(CNTYM*60.0))
      A = DT/DPART
      DO 65 JB = 1,NUMELM
      PARTCO(JB) = A * PARTCO (JB)
   65 CONTINUE
C
C CORRECTION OF THE COUNTS FOR THE DEAD TIME OF THE SAMPLE
C
      DO 100 JC = 1,NUMET
      FACT = 0.0
```

```
      FINCNT(JD) =  HICNT(JD)* FLXCOR
  150 CONTINUE
      WRITE (6,250)
  250 FORMAT ('0'/6X,'RESULTS'//6X'ELEMENT',7X,'UNCORRECTED COUNTS',8X,
     1'CORRECTED COUNTS')
      DO 300 M=1,NUMET
      WRITE(6,270)(ELNAME(M,N),N=1,3),HICNT(M),FINCNT(M)
  270 FORMAT ('0',6X,3A4,F11.0,16X,F10.0/)
  300 CONTINUE
  750 CONTINUE
      GO TO 10
  999 STOP
      END
```

APPENDIX C

ATMOSPHERIC PARTICULATE SAMPLES COLLECTED AT NARRAGANSETT, RHODE ISLAND

ATMOSPHERIC PARTICULATE SAMPLES COLLECTED AT NARRAGANSETT, R. I.

Sample No.	Sampling Date On	Sampling Date Off	Phosphorus Total P ng m^{-3}	Phosphorus Persulfate P, ng m^{-3}	Phosphorus Releasable Reactive P ng m^{-3}	Phosphorus Seawater Sol. P, ng m^{-3}	Sodium ug m^{-3}	Aluminum ng m^{-3}	Vanadium ng m^{-3}
1	10-24-75	10-25-75	17 ± 1	17 ± 1	6.3 ± 0.5	—	3.1 ± 0.3	690 ± 40	35 ± 2
2	10-29-74	10-30-74	6.3 ± 0.5	6.2 ± 0.5	3.6 ± 0.3	—	3.1 ± 0.3	250 ± 15	20 ± 1
3	10-31-74	11-1-74	31 ± 2	29 ± 2	16 ± 1	—	2.8 ± 0.2	680 ± 40	38 ± 2
4	11-6-74	11-7-74	22 ± 2	21 ± 2	11 ± 0.8	5.2 ± 0.4	2.5 ± 0.2	250 ± 15	35 ± 2
5	11-8-74	11-9-74	22 ± 2	—	6.5 ± 0.5	—	28 ± 2	480 ± 30	33 ± 2
6	11-21-74	11-22-74	6.0 ± 0.5	5.3 ± 0.4	1.6 ± 0.1	1.9 ± 0.2	9.2 ± 0.8	220 ± 13	5.2 ± 0.3
7	11-25-74	11-26-74	9.6 ± 0.8	8.2 ± 0.6	5.9 ± 0.5	6.3 ± 0.5	8.8 ± 0.7	210 ± 13	27 ± 2
8	11-26-74	11-27-74	6.8 ± 0.5	6.5 ± 0.5	2.6 ± 0.2	1.9 ± 0.2	3.3 ± 0.3	300 ± 20	11 ± 0.7
9	1-22-75	1-23-75	12 ± 1	10 ± 0.8	5.6 ± 0.5	—	3.9 ± 0.3	440 ± 30	34 ± 2
10	1-23-75	1-24-75	24 ± 2	24 ± 2	12 ± 1	—	3.6 ± 0.3	1200 ± 70	73 ± 4
11	1-26-75	1-27-75	7.2 ± 0.7	6.0 ± 0.5	2.1 ± 0.2	—	6.4 ± 0.5	350 ± 20	9.2 ± 0.5
12	1-30-75	1-31-75	7.7 ± 0.7	5.2 ± 0.5	2.4 ± 0.2	—	1.0 ± 0.1	360 ± 20	21 ± 1
13	1-31-75	2-2-75	4.3 ± 0.4	—	3.6 ± 0.3	—	1.5 ± 0.1	300 ± 20	25 ± 2
14	2-2-75	2-3-75	–	5.3 ± 0.4	2.1 ± 0.2	—	0.30 ± 0.03	290 ± 20	9.9 ± 0.6
15	2-19-75	2-20-75	22 ± 2	18 ± 1	2.6 ± 0.3	—	0.72 ± 0.06	720 ± 40	15 ± 1
16	2-20-75	2-21-75	13 ± 1	12 ± 1	7.4 ± 0.6	—	2.2 ± 0.2	1300 ± 80	23 ± 1
17	2-25-75	2-26-75	12 ± 1	11 ± 1	3.4 ± 0.3	—	8.8 ± 0.7	710 ± 40	10 ± 0.6
18	2-26-75	2-27-75	11 ± 1	12 ± 1	3.8 ± 0.4	—	3.4 ± 0.3	1200 ± 70	6.6 ± 0.4
19	2-27-75	2-28-75	10 ± 0.8	6.7 ± 0.7	2.7 ± 0.3	—	0.63 ± 0.05	490 ± 30	10 ± 0.6
20	2-28-75	3-1-75	5.3 ± 0.5	3.6 ± 0.3	3.6 ± 0.3	—	2.8 ± 0.2	430 ± 25	9.1 ± 0.6
21	3-1-75	3-2-75	13 ± 1	9.9 ± 0.8	2.1 ± 0.2	—	0.86 ± 0.07	200 ± 10	13 ± 0.8
22	3-3-75	3-4-75	7.5 ± 0.7	7.5 ± 0.6	2.6 ± 0.3	—	1.1 ± 0.1	700 ± 40	6.6 ± 0.4
23	3-4-75	3-5-75	20 ± 2	18 ± 1	2.6 ± 0.3	—	1.2 ± 0.1	460 ± 30	14 ± 0.8
24	3-5-75	3-6-75	14 ± 1	—	7.1 ± 0.5	—	2.0 ± 0.2	690 ± 40	24 ± 1

ATMOSPHERIC PARTICULATE SAMPLES COLLECTED AT NARRAGANSETT, R.I.
(continued)

Sample No.	Sampling Date		Phosphorus				Sodium	Aluminum	Vanadium
	On	Off	Total P, ng m^{-3}	Persulfate Releasable P, ng m^{-3}	Reactive P, ng m^{-3}	Seawater Sol. P, ng m^{-3}	µg m^{-3}	ng m^{-3}	ng m^{-3}
25	3-6-75	3-7-75	17 ± 1	17 ± 1	7.5 ± 0.6	—	4.1 ± 0.3	530 ± 30	20 ± 1
26	3-8-75	3-9-75	11 ± 0.9	11 ± 0.8	1.2 ± 0.1	5.0 ± 0.4	14 ± 1	820 ± 50	6.0 ± 0.4
27	3-9-75	3-10-75	9.3 ± 0.7	8.4 ± 0.6	1.6 ± 0.1	2.9 ± 0.3	1.9 ± 0.2	610 ± 40	14 ± 1
28	3-11-75	3-12-75	7.8 ± 0.6	7.1 ± 0.5	4.4 ± 0.3	5.2 ± 0.4	4.0 ± 0.3	230 ± 14	28 ± 2
29	3-13-75	3-14-75	15 ± 1	12 ± 0.9	3.0 ± 0.3	4.4 ± 0.3	5.9 ± 0.5	360 ± 20	20 ± 1
30	3-16-75	3-17-75	19 ± 1	19 ± 1	6.3 ± 0.5	6.9 ± 0.6	3.4 ± 0.3	850 ± 50	43 ± 3
31	3-18-75	3-19-75	-	4.2 ± 0.3	2.0 ± 0.2	-	5.3 ± 0.9	110 ± 10	2.8 ± 0.5
32	3-19-75	3-20-75	2.2 ± 0.3	1.2 ± 0.1	1.0 ± 0.1	-	14 ± 1	60 ± 5	0.6 ± 0.1
33	3-20-75	3-21-75	8.9 ± 0.7	4.8 ± 0.4	2.5 ± 0.2	1.7 ± 0.2	24 ± 2	250 ± 15	3.3 ± 0.2
34	3-21-75	3-22-75	7.7 ± 0.6	5.7 ± 0.5	2.8 ± 0.2	1.7 ± 0.2	3.2 ± 0.3	400 ± 25	19 ± 1
35	3-22-75	3-23-75	5.9 ± 0.5	5.3 ± 0.4	3.1 ± 0.3	3.2 ± 0.3	7.0 ± 0.6	150 ± 10	14 ± 0.8
36	3-23-75	3-24-75	5.5 ± 0.5	4.0 ± 0.5	-	1.7 ± 0.2	1.1 ± 0.1	340 ± 20	8.5 ± 0.5
37	3-24-75	3-25-75	7.5 ± 0.6	5.9 ± 0.5	6.2 ± 0.5	5.4 ± 0.4	3.7 ± 0.3	160 ± 10	42 ± 2
38	3-25-75	3-26-75	9.8 ± 0.7	7.0 ± 0.5	-	-	5.4 ± 0.5	470 ± 30	36 ± 2
39	3-26-75	3-27-75	18 ± 1	15 ± 1	3.7 ± 0.3	2.8 ± 0.2	4.5 ± 0.4	900 ± 55	5.6 ± 0.3
40	4-30-75	5-1-75	13 ± 0.9	6.9 ± 0.5	5.1 ± 0.4	4.0 ± 0.3	2.3 ± 0.2	500 ± 30	9.3 ± 0.6
41	5-1-75	5-2-75	9.9 ± 0.7	4.4 ± 0.4	3.4 ± 0.3	2.9 ± 0.2	3.8 ± 0.3	430 ± 25	3.4 ± 0.2
42	5-5-75	5-6-75	8.6 ± 0.6	4.6 ± 0.4	3.3 ± 0.3	3.3 ± 0.3	16 ± 1	260 ± 15	11 ± 0.7
43	5-12-75	5-13-75	11 ± 0.8	6.1 ± 0.5	4.2 ± 0.3	-	6.0 ± 0.5	590 ± 35	4.6 ± 0.3
44	5-13-75	5-14-75	12 ± 0.9	7.4 ± 0.6	4.5 ± 0.4	-	1.6 ± 0.1	460 ± 30	8.8 ± 0.5
45	5-14-75	5-15-75	19 ± 1	13 ± 1	5.3 ± 0.4	-	2.5 ± 0.2	1500 ± 90	15 ± 0.9
46	5-15-75	5-16-75	9.6 ± 0.8	5.4 ± 0.4	4.0 ± 0.3	3.6 ± 0.3	2.3 ± 0.2	190 ± 10	4.4 ± 0.3
47	5-16-75	5-18-75	27 ± 2	16 ± 1	-	-	2.4 ± 0.2	370 ± 20	8.1 ± 0.5
48	5-18-75	5-19-75	7.0 ± 0.6	3.9 ± 0.3	3.0 ± 0.2	-	3.2 ± 0.3	230 ± 10	13 ± 0.8

ATMOSPHERIC PARTICULATE SAMPLES COLLECTED AT NARRAGANSETT, R.I.
(Continued)

Sample No.	Sample Date		Phosphorus				Sodium	Aluminum	Vanadium
	On	Off	Total P ng m^{-3}	Persulfate Releasable P, ng m^{-3}	Reactive P ng m^{-3}	Seawater Sol. P, ng m^{-3}	µg m^{-3}	ng m^{-3}	ng m^{-3}
49	7-22-75	7-23-75	36 ± 3	20 ± 1	14 ± 1	8.8 ± 0.7	3.2 ± 0.3	230 ± 10	13 ± 0.8
50	7-28-75	7-29-75	32 ± 2	-	-	-	1.2 ± 0.1	400 ± 25	7.5 ± 0.5
51	7-30-75	8-1-75	31 ± 2	20 ± 1	15 ± 1	-	2.5 ± 0.2	1100 ± 70	21 ± 1
52	8-12-75	8-13-75	32 ± 2	21 ± 2	11 ± 1	-	-	-	-
53	8-14-75	8-15-75	37 ± 3	16 ± 1	7.2 ± 0.6	8.5 ± 0.7	1.6 ± 0.1	1400 ± 80	8.2 ± 0.5
54	9-16-75	9-18-75	19 ± 1	12 ± 0.9	3.6 ± 0.3	3.0 ± 0.2	1.2 ± 0.1	440 ± 30	16 ± 1
55	9-22-75	9-23-75	27 ± 2	16 ± 1	8.9 ± 0.3	-	0.80 ± 0.06	300 ± 20	9.3 ± 0.6
56	9-29-75	10-1-75	23 ± 2	12 ± 0.8	7.0 ± 0.6	4.0 ± 0.3	0.80 ± 0.06	240 ± 15	7.4 ± 0.4
57	10-13-75	10-15-75	26 ± 2	21 ± 2	15 ± 1	-	0.60 ± 0.05	570 ± 35	11 ± 0.7
58	10-21-75	10-23-75	35 ± 2	23 ± 2	14 ± 1	-	1.6 ± 0.1	670 ± 40	18 ± 1
59	10-27-75	10-28-75	23 ± 2	20 ± 1	10 ± 0.9	8.1 ± 0.7	1.9 ± 0.2	370 ± 20	19 ± 1
60	11-4-75	11-6-75	20 ± 1	9.2 ± 0.7	5.2 ± 0.4	7.7 ± 0.6	0.50 ± 0.04	670 ± 40	9.1 ± 0.5

APPENDIX D

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