SEAREX

SEA-AIR EXCHANGE

A proposal submitted to the

National Science Foundation

Office of the International Decade

of Ocean Exploration

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by

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SEAREX OVERVIEW

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ABSTRACT

The general objectives of the SEAREX Program are (1) the quantitative measurement of atmospheric fluxes of selected heavy metals (e.g., Pb, Cd, Zn, Se, Sb, As, Cu, Hg, Ag), ^{210}Pb and its daughter ^{210}Po and organic compounds such as the man-associated PCB, DDT, polynuclear aromatic and aliphatic hydrocarbons, phthalate plasticizers and the natural occurring steroidal and terpenoid hydrocarbons, fatty acids and alcohols, low molecular weight compounds such as ketones, aldehydes, and carboxylic acids to the ocean surface, (2) the identification of the sources for these substances in the marine atmosphere and (3) the investigation of mechanisms of exchange of these substances across the sea/air interface.

SEAREX OVERVIEW

(INCLUDING DETAILS OF MAJOR JOINT FIELD EXPERIMENTS)

I. INTRODUCTION

There has been increasing interest in the possibility that significant quantities of both natural and anthropogenic substances may be transported to the ocean via the atmosphere in mid-ocean regions. An understanding of the importance of the atmosphere as a transport path is critical in determining the basic geochemical cycles and budgets of a variety of naturally occurring substances and in predicting the near-global impact of anthropogenic material in open ocean regions.

In coastal areas primary attention has been given to direct water discharge of river and of urban and industrial wastes, although atmospheric input may also be large and in some cases dominant for certain substances. For example, the input of several trace metals to Lake Michigan appears to be primarily from air pollution fallout from Chicago (Skibin et al., 1973). Patterson and Settle (1974) found that the atmospheric deposition of Pb into a 12000 Km^2 area of the Southern California Bight accounted for about 45% of the pollutant Pb input, the remaining 55% being from waste water, storm runoff, and river input.

There is evidence that measurable quantities of lead and perhaps other trace metals, DDT, PCB, low molecular weight petroleum hydrocarbons and other organic substances are transported to the open ocean by the atmosphere, either as particles or in the gas phase (SCEP, 1970; FAO, 1971; Duce et al., 1976a; Fitzgerald, 1976; Bidleman et al., 1976). The high lead content of Greenland ice has been attributed to the burning of tetraethyl lead in auto-

mobile fuel in populated areas of the northern hemisphere, as has the atmospheric lead concentration over the central Pacific Ocean (Murozumi et al., 1969; Chow et al., 1969; Hoffman et al., 1972), and the North Atlantic (Duce et al., 1976a). High concentrations of atmospheric vanadium in particles in the tropospheric westerlies over the North Atlantic are believed to result from the burning of heavy fuel oils rich in vanadium porphyrin complexes on the North American continent (Duce and Hoffman, 1976). DDT and PCB are known to be present in the atmosphere over the North Atlantic in both the vapor phase and on particles (Bidleman and Olney, 1974; Harvey and Steinhauer, 1974). It is clear that the long-range atmospheric transport of many substances, both gaseous and particulate, has been well documented.

While we have now obtained some information on the concentrations and time variations of some of these substances in the marine atmosphere in locations such as Bermuda and Oahu, Hawaii, (and a few measurements from Samoa) as a result of studies supported by the NSF-IDOE/Pollutant Transport Program (PTP), there has as yet been virtually no information obtained on the flux of these substances into the ocean by rainfall, dry deposition and direct gas exchange. Until these measurements are made it will be impossible to assess the importance of the atmospheric transport of these substances in terms of their environmental cycles.

The increasing interest in atmospheric transport of both anthropogenic and natural trace substances to marine areas was highlighted by a recent workshop sponsored by SCOR and the U.S. National Academy of Sciences. This workshop on "Tropospheric Transport of Pollutants to the Ocean" was held in Miami in December, 1975. The results of the deliberations of participants at this workshop will be published later this year by the NAS. Discussions at the

workshop quickly uncovered our almost total ignorance of the fluxes of trace metals and virtually all organic substances between the atmosphere and the ocean, the mechanisms of exchange of these substances across the sea/air interface, and the great difficulty in distinguishing between natural and pollution sources for many of the trace substances found in marine air. There was a general concensus that a major coordinated research program investigating these sea/air exchange problems should be undertaken. This proposal for a sea/air exchange (SEAREX) program represents an initial step in that direction.

The purpose of this overview section is to put the entire SEAREX proposal into perspective, presenting our overall objectives, how the proposal was developed, the planned scope of SEAREX over its presently conceived five year duration, and a more detailed description of the first two year's work. Particular attention will be given to the need and rationale for common facilities and experiments. Subsequent sections deal with the investigations of the individual research groups in much more detail and the final section considers the management and field support functions in SEAREX.

II. OBJECTIVES OF SEAREX

The general objectives of the SEAREX Program are:

1. The quantitative measurement of atmospheric fluxes of selected heavy metals (e.g., Pb, Cd, Zn, Se, Sb, As, Cu, Hg, Ag), ^{210}Pb and its daughter ^{210}Po and organic compounds such as the man-associated PCB, DDT, polynuclear aromatic and aliphatic hydrocarbons, phthalate plasticizers and the natural occurring steroidal and terpenoid hydrocarbons, fatty acids and alcohols, low molecular

weight compounds such as ketones, aldehydes, and carboxylic acids to the ocean surface.

2. The identification of the sources for these substances in the marine atmosphere.
3. The investigation of mechanisms of exchange of these substances across the sea/air interface.

We propose a five year program to implement this study, with an initial two year funding period requested in this proposal. SEAREX will be undertaken as a closely coordinated field and laboratory study with common field and experimental facilities. Specifically, we propose:

1. To estimate from rain and dry deposition measurements the flux of heavy metals and organic substances during the wet and dry seasons at Tern Island, French Frigate Shoals in the North Pacific trades and at Tutuila Island, American Samoa in the South Pacific trades.
2. To investigate the importance of the ocean as a source for atmospheric heavy metals and organic substances through enrichment and fractionation effects occurring during the production of atmospheric sea salt particles by bursting bubbles. These studies will be undertaken using the Bubble Interfacial Microlayer Sampler (BIMS) developed at the University of Rhode Island (URI) in the earlier NSF/IDOE-PTP, together with an assessment of the natural occurrence of bubbles under varying conditions.
3. To evaluate the significance of soil and vegetation emissions, forest fires, and chemical manufacturing sites as sources of the volatile metals and organic substances found in the marine atmosphere.

4. To identify the natural or anthropogenic origin of Pb in marine aerosols by means of Pb isotope tracers and mass balance relationships of present atmospheric input fluxes with prehistoric sediment output fluxes.
5. To investigate in detail, using classical as well as sophisticated laser fluorescence techniques, the distribution and exchange between the particulate and vapor phase of organics and of the relatively volatile heavy metals such as Pb, Cd, Zn, Se, Sb, As, Cu, Hg, and Ag.
6. To investigate bubble surface area and volume spectra in the sea and the relative importance of single bubbles and bubble rafts as sources of atmospheric spray and sea salt particles, both as a function of wind speed.

We propose to undertake this sea/air exchange research program with a group of twelve senior co-investigators from eight institutions:

Dr. R. Chesselet, CFR/CNRS, France
Dr. R. Duce, University of Rhode Island
Dr. J. Fasching, University of Rhode Island
Dr. W. Fitzgerald, University of Connecticut
Dr. R. Gagosian, Woods Hole Oceanographic Institution
Dr. C. Giam, Texas A & M University
Dr. E. Goldberg, Scripps Institute of Oceanography
Dr. E. Kraus, University of Miami
Dr. C. Patterson, California Institute of Technology
Dr. J. Prospero, University of Miami
Dr. K. Turekian, Yale University
Dr. O. Zafiriou, Woods Hole Oceanographic Institution

The approximate budget breakdown for the first two years of SEAREX is given below. Details are presented in the individual proposals following.

Approximate Research Budget:

	1st Year	2nd Year
University of Rhode Island-University of Connecticut	$245,803	$241,800
California Institute of Technology	77,000	77,000
Scripps Institute of Oceanography	103,000	37,000
CFR/CNRS, France	25,000	25,000
Yale University	10,000	10,000
Woods Hole Oceanographic Institution	96,000	96,000
Texas A & M University	99,000	79,000
University of Miami	78,000	79,000
Approximate Field Support and Management Budget:	$137,080	$103,460

III. STRATEGIES FOR PROPOSAL DEVELOPMENT

The SEAREX Program is an outgrowth of several components of the Pollutant Transport Program (PTP) of the NSF/IDOE Environmental Quality Program. During the second PTP Workshop at Skidaway Institute of Oceanography in January, 1976, it was recommended that the study of pollutant transport into the ocean could perhaps be best structured around a series of investigations of the fluxes and processes of exchange across the major ocean/transport path interfaces, i.e., ocean/air; ocean/river; ocean/sediment; and ocean/biota. This concept was formalized by the NSF/IDOE Office during the summer of 1976 in a white paper entitled "Toward a New NSF/IDOE/EQ Program in Marine Pollution Studies".

In late summer, 1976, three of the PTP investigators (Duce, Goldberg, Patterson) studying sea/air exchange processes met in Paris to discuss a coordinated sea/air exchange program and strategies necessary to develop a

proposal for such a program, which would start on 1 October 1977, when the present PTP would terminate. A subsequent planning discussion was held between Goldberg, Duce and Dr. Thomas Church, NSF/IDOE program manager, at the Joint Oceanographic Assembly in Edinburgh in September, 1976.

To develop the strongest possible proposal, it was necessary to publicize SEAREX as widely as possible in the scientific community. In addition to individual contacts and letters, an advertisement soliciting letters of intent from the scientific community was published in Science in early November, 1976. Individuals interested in participating in SEAREX were asked to submit a five-page letter outlining their proposed program to an interim Scientific Advisory Committee. This Advisory Committee was composed of Dr. John Winchester, Florida State University; Dr. Karl Turekian, Yale University; Dr. Thomas Church, University of Delaware; Dr. Robert Duce, University of Rhode Island; Dr. Edward Goldberg, Scripps Institute of Oceanography; and Dr. Clair Patterson, California Institute of Technology.

Twenty three letter proposals were submitted and the Scientific Advisory Committee selected seven of these as being of high scientific quality and most compatible with the stated objectives of SEAREX. The investigators submitting these seven letter proposals met on January 7-8, 1977, at Scripps to develop the SEAREX proposal. At this meeting an important research area concerning Radon and the measurement of its radioactive daughters ^{210}Pb and ^{210}Po was identified. None of the letters of intention reviewed by the interim SEAREX Advisory Committee contained proposals to do these measurements. Karl K. Turekian volunteered to make these important measurements during the first week of January, 1977, and with the approval of the Advisory Committee an eighth investigator was included in the final SEAREX proposal.

IV. SCOPE OF THE FIVE YEAR PROGRAM

To attain the objectives outlined above a series of coordinated field experiments over a five year period are proposed. A timetable for this five year program is presented in Figure 1. Details concerning the various experiments are presented in Section V. of this overview and additional information is contained in the individual proposals which follow in later sections. The coordinated field experiments fall basically into two categories: (a) Flu experiments, where estimates of the atmospheric dry and wet deposition of the various chemical substances to the ocean surface are made from measurements in rain and dry deposition samples and (b) Source experiments, where the ocean is investigated as a source for these substances through the bubble breaking process using the Bubble Interfacial Microlayer Sampler combined with simultaneous bubble area/sea salt particle size and number distribution measurements, and where vegetation, soil emissions, and forest fires are investigated as a source for these substances in the atmosphere.

A. Flux Experiments

The initial flux experiment is designed to test the various meteorological, atmospheric sampling, and rain/dry deposition systems in an environment similar to open ocean conditions but located near participating laboratories and with relatively high expected concentrations and fluxes (thus minimizing analytical problems). This experiment will take place in May-June 1978 for three weeks, at Pigeon Key, Florida. The first remote field flux experiment will take place in the North Pacific at Tern Island, French Frigate Shoals, in the northwestern Hawaiian Islands (hereafter referred to as Hawaii). Site evaluation for this location will take place in October, 1977; construction of the tower and building facility in August-September, 1978;

b. Low Temperature Emissions from Forests and Agricultural Areas

Individual groups will collect atmospheric samples from forests, agricultural regions, etc. for analysis of organic substances and vapor phase metals, the latter by laser spectroscopy.

V. THE FIRST TWO YEARS OF SEAREX

A. Flux Experiments

1. Objectives

The objectives of the flux experiments are to give us quantitative information on the input of heavy metals and certain organic substances to the ocean from the atmosphere.

a. Heavy Metals

Heavy metals are a normal constituent of unpolluted air, and it is often not a simple matter, particularly in remote regions, to distinguish between natural and anthropogenic sources of these elements. A first approach to this problem has been to calculate enrichment factors using reference elements from expected sources such as the ocean or the earth's crust. This approach has identified, in several remote regions, the elements Pb, Cd, Zn, Se, Sb, As, Cu, Hg and Ag (Duce et al., 1976a) as having concentrations higher than normally expected from simple crustal weathering or bulk seawater injection into the atmosphere. Thus these metals are of primary interest, both because their high concentrations may be related to anthropogenic processes and because they may be related to natural geochemical processes which we do not yet fully understand. An estimation of the input to the ocean of these metals, and the clearly crustal origin elements as well, is critical to an understanding of the basic geochemical and environmental

the first Hawaii flux experiment (wet season) in February-March, 1979; and the second Hawaii flux experiment (dry season) in July-August, 1979.

In the third year the second set of flux experiments will take place in the southern hemisphere at American Samoa. Since the tower and building constructed and operated in 1976 as part of Duce, Fitzgerald, and Patterson's research in the PTP was considerably damaged by a hurricane in December, 1976, repairs and reconstruction of this facility will be necessary in the spring of 1980, but it is expected that the tower from Hawaii will be transported and reerected in Samoa in early 1980. The first Samoa flux experiment will probably take place in July-August, 1980, (dry season) and the second Samoa flux experiment in January-February, 1981, (wet season). If completion of the Hawaii field program and subsequent analyses will allow it, the Samoa experiments will be moved forward by about six months.

B. Source Experiments

1. Marine Sources - BIMS Experiment

The initial BIMS experiment will be a test investigation of the chemical measurements using BIMS coupled with bubble number/area measurements. This test experiment will take place on Narragansett Bay, Rhode Island in June, 1978. The first open ocean BIMS experiment will take place on R/V ENDEAVOR in the Caribbean in July, 1979. The second open ocean BIMS experiment will take place in the coastal upwelling region off Peru in the winter of 1980-81.

2. Continental Sources

a. Forest Fire Experiment

A specific forest fire experiment will take place at an as yet undetermined site in the western United States during the summer of 1981.