# Coastal Ocean Perspectives

Keynote Lectures presented as part of the Marine Sciences Research Center's "Coastal Summit"

# **MARINE SCIENCES RESEARCH CENTER**

STATE UNIVERSITY OF NEW YORK

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#### PREFACE

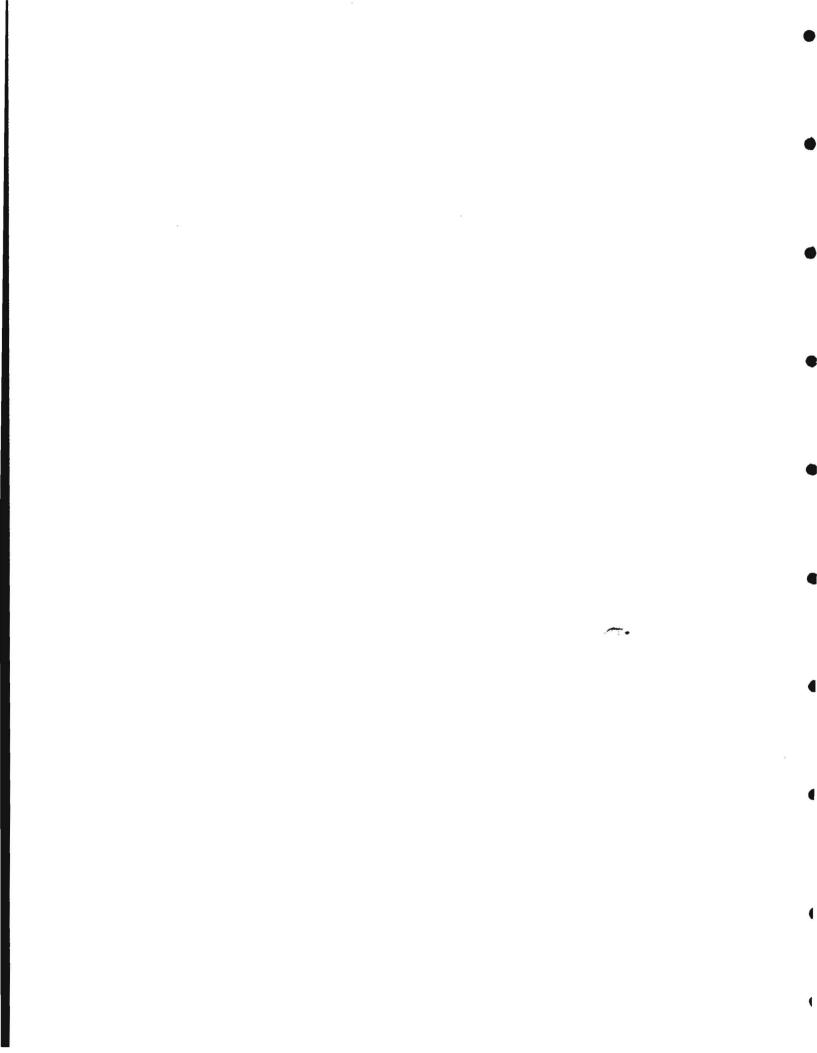
As part of the 25th Anniversary of the Marine Sciences Research Center, leaders in the fields of coastal marine science, management and global change met together in December, 1993, in a "Coastal Summit." The summit focused attention on indentifying the major existing and potential threats to the coastal ocean and developing strategies to eliminate those threats.

The topic was chosen because of MSRC's leadership in using science to develop strategies to allow humans to live in greater harmony with their environment. It was also chosen because of the growing threats to critical coastal ecosystems—more people than ever living near the coast, more reports of coastal degradation, and more developing countries unable to cope with these growing environmental stresses.

The scientists identified the major threats, both existing and looming in the future, to be nutrient pollution, chemical contamination, fresh water diversion, habitat destruction, over fishing, and microbial contamination. They also identified and explored a number of promising management strategies. These included tackling the most serious and irreversible threats first; organizing research efforts and management decisions on an integrated coastal management basis; taking full advantage of existing scientific knowledge and technology; using new monitoring technologies that can be employed in many places and under adverse conditions; and encouraging linkages among university scientists, engineers, government scientists and administrators, environmental managers, and non-governmental organizations.

To stimulate discussion during the Summit, and to provide a common frame of reference, several distinguished oceanographers were invited to present keynote lectures. These lectures are reproduced in this volume.

Thanks are due to Lori Palmer, Eileen Goldsmith and Trudy Bell for their help in producing this volume.



# **Coastal Ocean Chemistry**



Keynote Lectures presented as part of the Marine Sciences Research Center's "Coastal Summit"

# *Coastal Ocean Chemistry: 25 Years In the Cauldron*

#### by

## John W. Farrington Woods Hole Oceanographic Institution

#### INTRODUCTION

I am honored and pleased to be invited to share in your celebration of the twenty-fifth anniversary of the Marine Sciences Research Center (MSRC).

Professor Karl K. Turekian of Yale University, a scholar who has contributed substantially to our knowledge of coastal and estuarine geochemistry, provided us with a fine example of an understatement when he wrote about estuaries (and I submit that this applies to the other parts of the coastal oceans):

From the geochemical point of view, an estuary is a reaction vessel where the mixing of stream water and seawater has consequences far beyond simple dilution.... Turekian, 1977

A cauldron is a large kettle or vessel in which various ingredients are mixed and sometimes heated. We might think of an estuary and the coastal ocean as a series of giant cauldrons. Borrowing from Professor Turekian, the consequences of the inputs, fates, and effects of both chemicals mobilized by natural processes and modern civilization in these "cauldrons" have often been accompanied by heated debate in terms of policy and management issues.

My career in being active in the "cauldron" spans about 25 years from graduate student

research to the present. Thus, the title of my lecture. I will attempt to be global, retrospective, and set forth challenges for the future. In so doing, I have chosen a few examples of research by present MSRC marine geochemistry and chemical oceanography faculty as illustrations to pay deserving tribute to their efforts. Other examples are drawn from work in geographically nearby areas to illustrate the importance of MSRC to the state and regional coastal water quality efforts as well as to global issues.

I will avoid extensive referencing in the written version of this paper because of the nature of this "Summit." Since I will concentrate on organic compounds, I have worn an American Chemical Society tie displaying the periodic table of the elements in an attempt to satisfy those in the audience who have favorite trace metals and radionuclides!

#### The Past 25 Years

In 1972, the conference "The Water's Edge" (Ketchum, 1972) was held to identify critical problems of the coastal zone. The conference identified the basic biological, chemical, and physical research needed for wise use and management of the coastal zone. Such issues as transport, dispersion, upwelling, cycling of nutrients and of hazardous chemicals, surveillance of inputs of the various contaminants, effects of solid waste disposal, effects of chronic long-term sub lethal contaminants on

organisms and ecosystems and the assimilative capacity of the coastal zone for all kinds of waste were considered. Do these sound familiar?

Although still very important today, these are not new topics; we have been dealing with them for a long time. These are long-term problems and the question is, Are we making progress? The answer is yes! We are making progress in several areas, but we have to continue to be persistent, to be patient, and we cannot become complacent.

For example, since "The Water's Edge" conference, there has been a great deal of innovative research and new knowledge on the role of estuaries in the biogeochemical cycles of carbon, nitrogen, and sulfur (e.g. Brink et al. 1992; Brink 1993). We have new ways of looking at the coastal ocean and global ocean, for example, by using remote sensing. But the basic qualitative picture we get is that put together by the approaches available at the time of the "Water's Edge". The major difference has been an increase in our ability to provide quantitative and semi-quantitative assessments of biogeochemical processes in coastal ocean ecosystems. The present challenge is to become much more detailed and much more quantitative because of the concern about the global carbon cycle and the inter-relationships between the nutrients and the global carbon cycle.

#### Marine Organic Geochemistry

I am most intimately involved with the organic geochemistry aspects of biogeochemical cycles and thus will provide some examples of what I mean from that arena. Details of molecular and physical-chemical forms of organic matter have increased in importance, as discussed in an excellent chapter by Professor Cindy Lee of MSRC and her co-author, Professor Stuart G. Wakeham (Lee and Wakeham 1988). More recent workshop reviews are found in Farrington (1992) and Hedges and Lee (1993). Organic geochemists have been looking at the details of the cycling of organic material and, for some time, have been concerned about heteropoly-condensates or geopolymers. More recently, this has included concerns about colloidal organic material and colloids, but we still do not understand much of the formation mechanisms with respect to the colloidal organic naterial in the oceans. (e.g. Benner et al. 1992). There has been some interesting and exciting recent progress; for example the work by Professor Edward Goldberg and his colleague Mark Wells ( e.g. Wells and Goldberg 1991) and by Professor John Hedges and co-workers (e.g. Benner et al.1992).

Regarding the role of the oceans in cycling greenhouse gases, some of the pioneering work on methane in the ocean was done by Professor Mary Scranton of MSRC. Mary studied not only the question of methane that was produced by early diagenesis in the sediments. but the whole question of methane production in the water column itself. I had the pleasure of being her coworker in one of these early studies (Scranton and Farrington 1977).

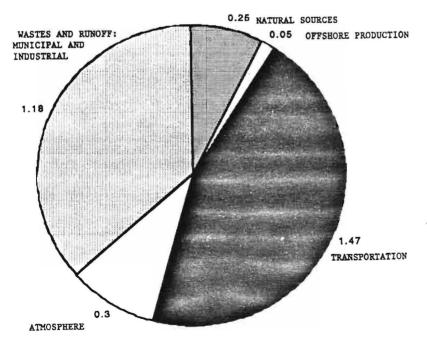
#### Chemicals of Environmental Concern

Another important focus for coastal ocean chemistry in the past 25 years has been chemicals of environmental concern. There are a wide range of chemicals that are mobilized or synthesized by our modern civilization. In fact, there are 10,000 to 100,000 or more organic chemicals of environmental concern.

Chemicals can be mobilized during coal mining, metal ore mining, oil and gas production, as well as during anthropogenic synthesis (for example, PCB's, DDT, kepone, and tributyltin). It is not the case that we have solved problems arising from contamination by those synthesized compounds. For example, both the work of Tanabe and his colleagues in atmospheric concentrations of DDT as well as other chemicals in the atmosphere and ocean (especially in southeast Asia, in the Indian Ocean) and studies by the World Health Organization show that these chemicals are present in mothers' milk, which indicates that DDT contamination continues to be a problem in developing countries (e.g. Tanabe, 1991).

We make a fundamental error by assuming that because we are managing these contaminants in the developed countries, we have solved the problems in a global sense. Indeed, an error

Figure 1. Petroleum Input to the Ocean (millions of metric tons per year).



sometimes made by policy makers is to say, "Scientists have pointed this problem out to us, we've reacted to it and it's over."

#### Oil inputs

Turning to the issues of oil inputs to the ocean, I believe too much attention is paid to spills like that of the Argo Merchant, or other types of oil spills, such as oil well blow-outs. Offshore wells are often located in shallow water and are of concern in coastal environmental quality considerations (e.g. NRC 1993). The argument is made that blowouts are unlikely to happen in developed countries because there is good regulation and good management for these wells. However, I don't think that is the case in a large proportion of the world's coastal waters. Today especially, wells are sited in the coastal waters of developing countries. It is a mistake to think that the rules and regulations of Europe, the United States, and Japan, for example, are applied, enforced, and supported by knowledgeable inspectors and monitoring programs in those sites to the extent that they are in the developed countries.

One of the common misperceptions about oil spills is that they are the most important input of oil to the marine environment. In fact, it is the chronic types of discharges, not only those associated with urban areas but also chronic discharges from offshore production activities in the coastal areas of developing countries, that are more important (Fig. 1).

#### Aromatic hydrocarbons

Perhaps the most important chemicals of environmental concern related to oil inputs to the oceans are the aromatic compounds. These includes the aromatic hydrocarbons with carbon and hydrogen as well as those compounds containing nitrogen, sulfur, or oxygen. We know there is significant input of aromatic hydrocar-

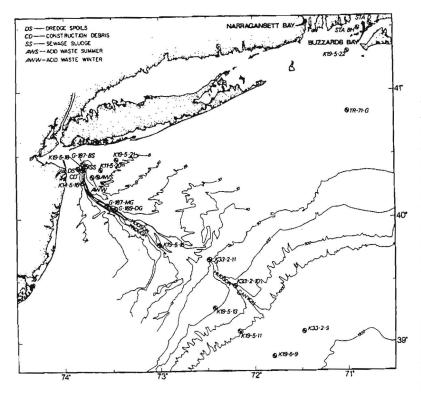


Figure 2. Chart of sampling stations reprinted from Geochimica et Cosmochimica Acta, Volume 41, Farrington and Tripp, Hidrocarbons in Western North Atlantic Surface Sediments, pp 1627-1641, copyright 1977, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X5 1GB, UK. bons from combustion of fossil fuels of various types — from forest and grass fires — as well as from petroleum spills, chronic sources, and naturally occurring seeps. Another source of polycyclic aromatic hydrocarbons to the marine environment is production during early diagenesis in sediments as a consequence of microbial reactions near the sediment-water interface.

The source of the hydrocarbons can be hotly debated, as I have noticed in the popular press reporting recent arguments of whether or not any oil from the *Exxon Valdez is* showing up in samples from Prince William Sound, Alaska. One view is that most of the hydrocarbons in sediments from Prince William Sound have come from oil seeps in the past or from previous spills, and not from the *Exxon Valdez* oil spill.

Some lessons learned in our work in the New York Bight come to mind when I hear and read about the controversy with the *Exxon Valdez* -Prince William Sound samples.

## Hydrocarbons in New York Bight Sediments:

Lessons for Monitoring

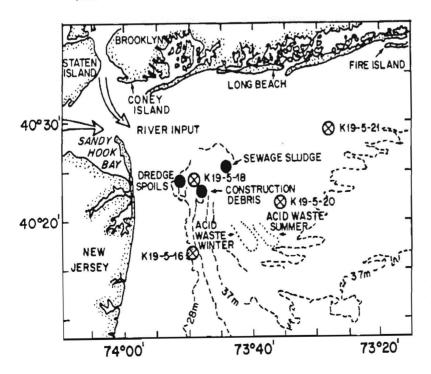
In 1972 and 1973, my research group and other colleagues collected surface sediment samples from the New York Bight as part of a larger effort of the International Decade of Ocean Exploration program, which focused on environmental quality and the oceans. Sampling station locations are given in Figures 2 and 3. We extracted the sediment samples with organic solvents and isolated the hydrocarbons. About 1.5 ml of liquid hydrocarbons were extracted from a kilogram of sediment, equivalent to one part per thousand in New York Bight surface sediments (Farrington and Tripp 1977). Since that time we, and several other research groups, have analyzed the aromatic hydrocarbons in other sediment samples and noted that all urban harbor areas and some dredge spoil disposal sites have very high concentrations of aromatic hydrocarbons.

One of the things we were asked to address at this Coastal Summit is monitoring, and so, I want to talk to you just a bit about a lesson that I hope we have learned. Monitoring for oil contamination in samples of tissues, sediments, or water requires a series of procedures: collecting a sample, extracting it, purifying the sample, and finally screening using a procedure like UV fluorescence. The result is an indication of the presence or absence of oil—a fairly crude procedure.

One can get approximate quantities from this procedure and it is relatively inexpensive. Detailed chemical analysis provides much better characterization of the compounds present, but is expensive. Intense debates have taken place in the international community about the best way to monitor for petroleum compounds in the environment. Because UV fluorescence was inexpensive, this was the technique that was first employed. A better approach is to go beyond UV fluorescence and use follow-up techniques to confirm the answer from the screening. In practice, however, very seldom have the followup techniques been employed. Can you get into trouble this way? The answer is, Yes.

As an example, I will return to our work in the New York Bight and describe additional work in that area in the late 1970s and 1980s (Farrington et al. 1983). We were interested in whether or not the aromatic hydrocarbons we had identified as present in high concentrations in sediments in our earlier studies were taken up in the tissues of polychaetes and other benthic animals. We sampled some worms and put the tissue through the screening procedure.

Figure 3. Chart of sampling stations from Farrington and Tripp (1977)



UV fluorescence screening indicated there were 1 to 10 parts per million aromatic hydrocarbons in the tissue of these polychaetes. If we had stopped there we would have made a terrible error. We used gas chromatographic analysis and found just one major peak in the gas chromatogram. I was reasonably convinced that the one major peak was the natural biosynthetic hydrocarbon squalene, present in many marine animals. Squalene would have been present in the aromatic hydrocarbon fraction, given our methods at that time, having a gas chromatographic retention time similar to that of the peak in the chromatogram.

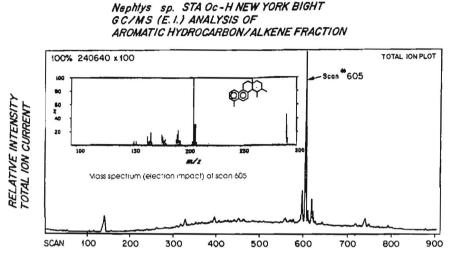
Further analysis of the fraction by gas chromatography-mass spectrometry-computer system revealed that the compound has two aromatic rings like naphthalene (Fig. 4). In fact, the compound is a microbial alteration product of a natural organic compound. The reason it exhibits a petroleum-like signal in the UV fluorescence techniques is that this particular compound looks like a substituted naphthalene, of which there are many in crude oils and several fuel oils.

We still don't know the origin of the compound and we don't know why the polychaetes have it in their tissues. Perhaps it is resistant to metabolism, whereas many of the other polycyclic hydrocarbons in the sediments of the New York Bight can be metabolized by the polychaetes. The important point of this result is that the 1 to 10 parts per million in polychaete tissue was not petroleum, but rather a product of early diagenesis in the sediments.

#### New Bedford Harbor and Buzzards Bay, Massachusetts Release of PCBs in Sediments

Let me go on from the New York Bight work to our work in Buzzards Bay and talk about another chemical of environmental concern,

Figure 4. GC/MS Chromatogram of Hydrocarbons in the Polychaete (worm) Nepthys species from the New York Bight Dump Sites. Reprinted with permission from Environmental Science and Technology. Farrington et al, copyright 1986, American Chemical Society.



PCB's, in New Bedford Harbor. The harbor sediments have PCB concentrations ranging from one part per thousand to hundreds of parts per million (on a dry weight basis). The harbor is a Superfund site and was identified as a problem area by scientific research conducted between 1974 and 1978. (e.g. Weaver 1982 and Farrington et al. 1983). Yet even at present, over fifteen years later, there is no clean-up or remediation procedure that is acceptable to influential groups of the general public.

The Environmental Protection Agency (EPA) was ready to incinerate the "hot spot" sediments, but recently, some of the citizen groups said that the EPA had not looked at any of the new remediation technologies. As a result of these concerns, the EPA had to postpone incineration. (As we go to press in July, 1994 with this article, remedial dredging of the hot spot and containment of the dredged sediments is underway).

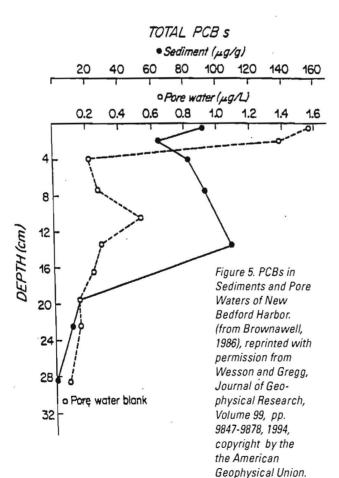
One of the questions is, Why do we have to worry about these particular sediments? The answer is that they are a continuing source of input. How much of the PCB's actually are released back to the overlying water column was the subject, in part, of a Ph.D. dissertation of Dr. Bruce Brownawell, now an Associate Professor here at MSRC.

Professor Brownawell looked at the concentrations of PCBs in sediments and showed that there were PCBs present in the pore water (Fig. 5; Brownawell and Farrington 1985, 1986; Brownawell 1986). He noticed that concentrations in the pore water were much above what we would expect in normal partitioning between solid phase and sea water, and argued that they probably were associated with colloids. Professor Brownawell undertook some very innovative research looking at the interaction between PCBs and colloids in the laboratory (Brownawell 1986) and showed that these hydrophobic compounds can be associated with colloids in the inter-stitial waters. These results have important implications on calculations of the flux of PCBs back to the overlying water column.

The release of chemicals of environmental concern from sediments once they are deposited is an important area for future research. It is particularly important because in many cases we are undergoing a transition in which inputs of these chemicals to the marine environment are no longer dominated by their initial or original sources, but rather by secondary sources such as release from sediments.

As an example, prior to the 1970s, PCB addition to the coastal ocean and estuarine area of New Bedford Harbor and Buzzards Bay, Massachusetts was dominated by runoff or direct effluent discharge (and perhaps atmospheric input), and these compounds were scavenged by particles and deposited in the sediments. Subsequently, the inputs were stopped by regulation, and now we have a reservoir of PCBs in the sediment, with a potential flux back to the overlying water column. How we deal with chemically contaminated sediments is one of the serious problems in marine pollution management and remediation of today and the next 10 to 20 years.

Leaving sediments in place, using bioremediation, and dredging all have been considered. It is important to note that many developing countries are dealing with the initial



input of chemicals and have yet to make the transition to the phase in which the inputs have been stopped. An additional important point regarding sediments contaminated with chemicals of environmental concern is that more work must be done on the bioavailability of the contaminants.

As an example of the way this might be approached, my student Susie McGroddy and I have studied PAHs and PCBs in Boston Harbor sediment (McGroddy 1993; McGroddy et al., 1995). In general, we measured about one part per million (mg per gram dry weight) of PAHs in the sediments, although the same areas in the harbor have concentrations about 10 times to 100 times greater. The pore water has elevated concentrations of several of these compounds, including pyrene.

We have modeled these results taking into account the presence of PAHs in solution, associated with colloids, and sorbed to the sediment surfaces. We have estimated what fraction of the PAHs are actually available for easy exchange into the pore water as compared to those that can be extracted chemically from the sediment. This is important because conclusions on bioavailability often are based on total concentrations of individual compounds in the solid phase in the sediments determined by chemical extraction methods, as has been the case for early versions of Sediment Quality Criteria set forth by the U.S. Environmental Protection Agency. What is needed is an assessment of the fraction of the total PAHs that are available for rapid exchange into the water and, thereby, potentially available for biological uptake. The next step in this work is relating the fraction available for rapid exchange with that actually taken up by organisms.

### Monitoring for Chemicals of Environmental Concern and Interactions with Research

The type of work I have been describing would not have been possible without applying advances in analytical chemistry of the past 25 years to coastal and estuarine environmental quality considerations. The advances have been substantial, to the point that some critics, with whom I disagree, say that the only problem with environmental chemicals in the coastal ocean and estuaries is the fact that chemists are able to measure very low concentrations! Applying these advances must go hand-in-hand with giving greater attention to quality control and quality assurance.

These issues are often considered boring and dull for research scientists; at least this seems to be true given the difficulty of getting research scientists to participate in quality control and quality assurance studies. Part of the difficulty is the lack of good standard reference materials with which to check our measurements of these chemicals of environmental concern. Even when standards are available (e.g. from the National Institute of Standards and Technology), they are often available in limited quantities such that the demand exceeds supply. This problem makes comparison and calibration difficult; hence quality assurance and quality control suffer.

In addition to recent advances in the geochemistry of organic compounds in the coastal environment, in the past 25 years we have seen significant advances in understanding estuarine biogeochemical processes, in general. In particular, our knowledge of what goes on in sediments during the early diagenesis of organic matter, including our understanding of microbial processes and animal-sediment interactions, has increased tremendously. The uses of the uranium decay-series radionuclides and other natural radionuclides as tracers for estuarine sediment dynamics have been truly spectacular in the last 25 years. Professors Robert Aller and Kirk Cochran, both of MSRC have been pioneers in these research efforts. This field of research is critical to answer questions re-garding the fate of contaminants associated with sediments if the overlying water column is oxic and benthic animals are living in and mixing the sediments.

Our insights into estuarine biogeochemical processes have been gained partly through the use of controlled ecosystems or mesocosm experiments. For example, the CEPEX and MERL studies, allowed us to manipulate the system in ways not possible in the natural environment and provided the types of controls that we needed to interpret the field data. We must continue to integrate field, laboratory, and mesocosm studies and couple this knowledge with our understanding of the behavior of organic chemicals of environmental concern.

Important consequences of advances in fundamental research in coastal biogeochemistry are the insights they give us into creating better monitoring programs. It is critical that we achieve an appropriate balance between research and monitoring for more effective management of the coastal ocean. A good example of such a balance is the U.S. Environmental Protection Agency Mussel Watch program, pioneered by Professor Edward Goldberg many years ago. From its inception, this program maintained that research was a part of monitoring and that a close connection must be maintained between them. (Farrington, 1983).

The International Mussel Watch, also proposed by Professor Goldberg in 1975, is finally happening (Farrington and Tripp 1993). Collections of mussels have now been made at stations in South and Central America, and the

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results of the analyses will be available shortly. In each case local scientists were, or are, involved in identifying appropriate sampling stations and in interpreting the data. Both scientists and coastal zone managers are now discussing how to use this information for more effective management of the coastal ocean. These types of interactions — between scientists in developed and developing countries and between scientists and managers — must be encouraged and sustained, not simply for the duration of any one program, but for the longer term.

Another aspect of monitoring in which scientists play a critical role is in the development of appropriate field instrumentation. In the past 25 years we have seen significant progress in our ability to measure basic properties of sea water (e.g., using salinitytemperature and dissolved oxygen probes). We must improve our ability to make chemical measurements on appropriate time and space scales in the coastal ocean. Effective monitoring of the coastal ocean requires being able to obtain measurements during adverse conditions such as storms. This will require robust moorings as well as improvements in automated technology and remotely operated vehicles (ROVs) and autonomous underwater vehicles (AUVs).

While we must encourage appropriate monitoring and a more effective link between research and monitoring, it is important to emphasize that we must continue to receive adequate funding for fundamental research in the coastal ocean. Perhaps the most important reason is that the research results that we apply to management decisions today are based on work carried out in the past 20 years or so.

One of the critical problems in coastal ocean management is the mismatch between the expectations of policy makers and managers on the one hand, and scientists on the other in terms of how long scientists need to work on a problem, how much funding is needed to solve it, and how quickly the data can be used to provide more effective management tools.

One way to address these expectation vs. reality problems, as well as to strengthen the link between research, monitoring, and management, is through education. We need to be doing much more of this - not just discussions with legislators and not just with adults - but also making a concerted effort to educate young people and the general public about the ways science and policy can interact. For example, the Woods Hole Oceanographic Institution has a program designed to bring high school teachers to Woods Hole to get an insight into what it means to do research and how research results might be used. They also discuss how research interacts with public policy at the local level.

l close this lecture with a quote from Dr. Gro Harlan, Bruntland, Chair of the Commission of Environment and Development: "Our consideration of the environment will have to become the essence of political forethought." As political leaders follow the advice of this quote, they depend on scientists, such as many in this room, to communicate what we know and what we believe, and to have input into the policy process. If we understand that this is the world in which we must operate as scientists, I think we will be well served.

#### ACKNOWLEDGMENTS

I appreciate the patience of the MSRC-SUNY Faculty and Staff in receiving my revised manuscript from the meeting. Unexpected illness played havoc with my schedule. I have been fortunate in my career to interact with many wonderful colleagues, students, and postdoctoral associates, and to have benefited from public and private funding from a variety of agencies and sources. Most important I have enjoyed the support and love of my wife Shirley, daughter Karen, and son Jeff.

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Wells, M.L. and E.D. Goldberg (1993) Colloid Aggregation in seawater. Marine Chemistry: 41: 353. JOHN FARRINGTON is a true New Englander, whose academic career has kept him close to his roots. He received his B.S. and M.S. in chemistry from Southeastern Massachusetts University and his Ph.D. from the University of Rhode Island. He joined the Woods Hole Oceanographic Institution (WHOI) as a postdoctoral fellow in the chemistry department and advanced through the ranks from Assistant to Associate to Senior Scientist.

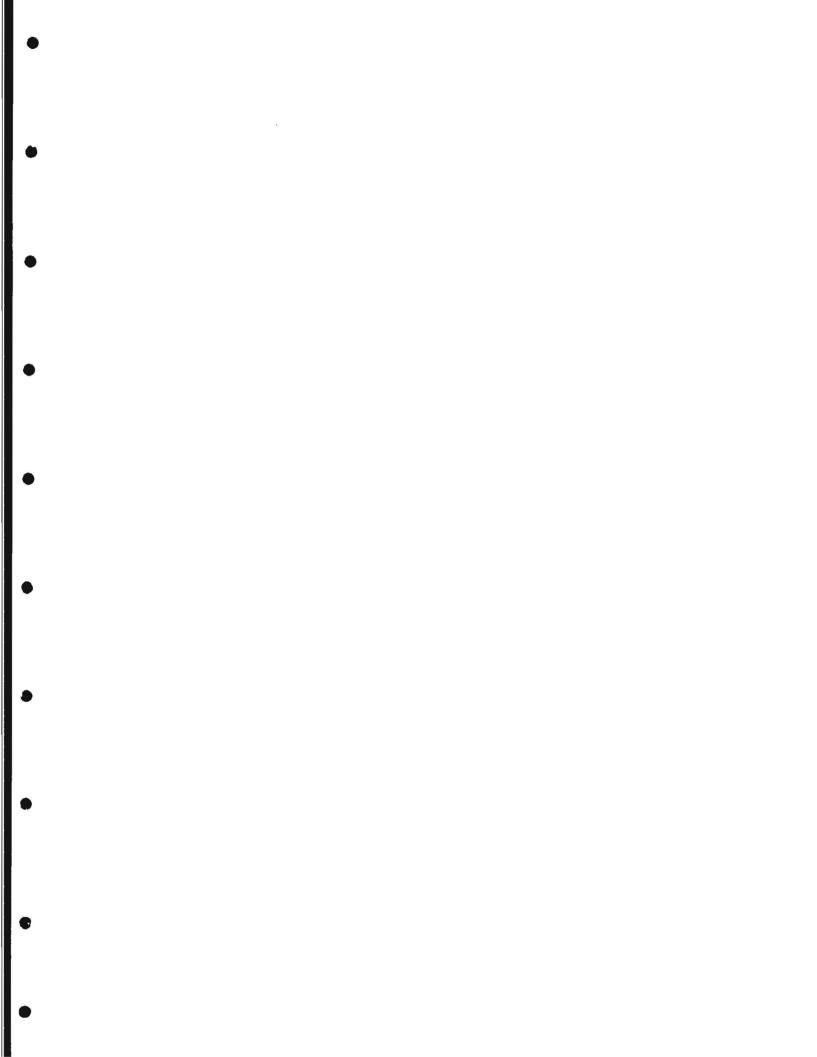
In 1988, Dr. Farrington left (WHOI) to become the Michael P. Walsh Professor and Director of the Environmental Sciences Program at University of Massachusetts-Boston. He returned two years later to his present position of Associate Director for Education and Dean of Graduate Studies.

His longstanding research interests lie in the organic geochemistry of the marine environment, and his professional interests include science-policy interactions and education in the marine and environmental sciences.

Dr. Farrington serves on a number of editorial boards and national and international committees, including UNESCO's Group of Experts on Methods, Standards, and Intercomparisons and the National Research Council Committee on Coastal Oceanography.

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