Measurement Technology Development for Marine Pollution Vol. II

The MITRE Corporation

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ABSTRACT

The MITRE Corporation, under a grant from NOAA's Office of Ocean Engineering, has prepared this two volume study to provide background support in efforts to develop technology for NOAA's marine pollution programs. Volume I of the study includes a survey of pollution measurement requirements, measurement technologies currently in use, the limitations of this existing technology, and the role of emerging laboratory, in situ, and remote sensing technologies in future NOAA programs. Volume II provides an overview of current NOAA programs related to marine pollution monitoring in the mid-Atlantic region, as well as a detailed survey of emerging technology for laboratory and in situ marine pollution measurements.

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INTRODUCTION

This volume of three appendices provides background material for Volume I. Appendix A describes NOAA marine pollution programs in the Mid-Atlantic Bight in detail. Appendix B provides a detailed survey of emerging laboratory and *in situ* measurement technology. Appendix C is a compilation of standard analytical laboratory methods relevant to NOAA marine pollution programs.

APPENDIX A

NOAA MARINE POLLUTION PROGRAM OF THE MID-ATLANTIC REGION

A.1 INTRODUCTION

It has been recognized within NOAA that a major, long-term effort is required to address and coordinate research and monitoring activities in the Northeast Atlantic region. NOAA management is actively attempting to assemble an integrated program for this area. At this time, the Northeast Fisheries Center is responsible for planning and managing research and monitoring. Important research and service functions are being supplied by the Research and Development and Oceanic and Atmospheric Services arms of NOAA.

NOAA marine pollution-related research, development, and monitoring activities involve three major line components (MLCs). These are: the Office of Fisheries, Office of Oceanic and Atmospheric Services, and the Office of Research and Development. The programs actively engaged in such studies in the Mid-Atlantic Bight are: 1) The Ocean Pulse Program (Office of Fisheries); 2) The Marine Ecosystems Analysis (MESA) Program (Office of Research and Development); 3) The National Ocean Dumping Program (Office of Oceanic and Atmospheric Services); and 4) The Marine Resources Monitoring Assessment Prediction (MARMAP) Program (Office of Fisheries).

The material included in this Appendix identifies objectives, special environmental issues and concerns addressed by each of the NOAA programs and provides a review of the research and monitoring strategies currently being implemented. This information was derived from current NOAA documents as well as from the findings of a sequence of interviews with NOAA program managers during August and September, 1979.

A.2 THE NEW YORK BIGHT PROJECT

The New York Bight Project Office at Stony Brook, New York has been a major effort of NOAA's Marine Ecosystems Analysis (MESA) Program, within the Office of Marine Pollution Assessment. The Project received initial funding in 1973 and has conducted multi-disciplinary research to examine the condition of the New York Bight ecosystem and identify its environmental problems.

A.2.1 Project Objectives

The Project, presently scheduled for completion by the conclusion of FY 1981, has been charged with designing, testing and evaluating a monitoring program for the New York Bight. As a result, the personnel involved in the project are particularly knowledgable of the observational requirements appropriate to marine pollution in that region.

The principal objectives of the monitoring program are: 1) to continually diagnose the health of the New York Bight ecosystem, and 2) predict the response of the ecosystem to environmental variables. Monitoring findings would provide the basis for environmental management and control decisions for the New York Bight. The start-up cost for the New York Bight Monitoring Project was approximately $240K;

ongoing yearly cost is about $445K. Overall MESA funding in FY 1978 was $8.35M.

A.2.2 Project Description

The Project is to make use of current knowledge and information on pollution distribution and impacts and will not be directed toward proving ecosystem cause-effect relationships. In order to organize this existing information, a "state-of-the-art synthesis" is being conducted to examine the interaction of ecosystem components which result in observed conditions in the Bight. The synthesis is to be completed by the end of FY 1981. Revisions in the monitoring program will be appropriately guided by findings of the information synthesis. This approach parallels the intent of the MITRE study for NOAA. It is MITRE's approach to make recommendations for technology needs and sampling strategies based on reported cause and effect relationships among the pollutants and ecosystem elements.

A.2.2.1 Measurement Program. The monitoring envisioned by the MESA program management will involve the measurement of 1) independent variables (e.g., heavy metals, temperature, pesticides, etc.); 2) influential factors (e.g., wind intensities, currents); 3) effects where cause-effect is known (e.g., population decrease of organisms due to oxygen depletion events); and 4) responses where cause-effect is not known (e.g., decline in faunal diversity). Emphasis of the monitoring effort is to be placed on the first, second and fourth approaches; the third approach is to be implemented in cases where unique cause-effect relationships are recognized. From previous experience and observation, numerous environmental concerns and disturbances have been recognized in the New York Bight ecosystem. Surveillance monitoring of these potentially recurring problems is to be maintained as part of the program. Table A-1 lists these environmental concerns and the corresponding time-frame during which significant changes could occur or the season during which the phenomenon is of concern.

Each of these concerns, with the exception of modification of fish distributions, has been translated into a set of parameters to be monitored, as shown in Table A-2.

Table A-2 lists environmental concerns and associated parameters with corresponding sampling frequency to be applied for each. Parameters of interest and sampling frequency will be subject to revision as a result of research efforts, information synthesis activities, and test and evaluation of the monitoring program.

As a result of a MESA-sponsored assessment of available information about the physical and chemical behavior of dredged materials in the ocean, new studies of dredged material dumping in the New York Bight have been initiated. These investigations include:

1) Detailed examinations during FY 1978 of the composition of dumped dredged materials with special emphasis applied to metals and organic compounds.

2) Examination during FY 1979 of physical and chemical processes operating during dredged material dumping to elucidate environmental fates of contaminants introduced by such dumping.

TABLE A- 1

INDICATORS OF MARINE POLLUTION

Environmental Concern	Period of Immediate Interest
Nearshore water quality	Short-term (biweekly)
Oxygen depletion	Seasonal (April to September)
Modification of fish distributions	Long-term (semi-annual)
Degraded benthic communities	Long-term (semi-annual)
Chemical contamination of fishes and shellfishes	Long-term (semi-annual)
Pathogenic contamination of shellfish	Long-term (semi-annual)
Contaminated sediments	Long-term (annual)

TABLE A-2

PARAMETERS AND SAMPLING FREQUENCY FOR THE
NEW YORK BIGHT MONITORING PROJECT

Environmental Concern/Response	Parameter	Sampling Frequency
Nearshore Water Quality	Dissolved Oxygen	Bi-weekly
	Nutrients	"
	Turbidity	"
	Coliform	"
	Floatables	"
	Temperature	"
	Salinity	"
Oxygen Depletion	Dissolved Oxygen	4 times/year (seasonal
	Temperature	"
	Salinity	"
	Nutrients	"
	Plankton	"
	Currents	Continuous
Contaminated Sediments	Cadmium	Annual
	Mercury	"
	Coliform	"
	TOC	"
	Artifacts	"
	PCB	"
	Coprostanol	"
	Plutonium*	Every 3 years
Degraded Benthic Communities	Abundance	Semi-annual
	Diversity	"
	Gill Clogging	"
Contamination of Demersal Fishes and Shellfish	<u>Fishes</u>	
	Cadmium	Semi-annual
	Mercury	"
	PCH	"
	PNAH	"
	<u>Shellfish</u>	
	Cadmium	"
	Mercury	"
	Coliform (total, fecal, E. coli)	"
	Pathogens	
	Fecal Strept.	"
	Salmonella	"
	Claust. Perf.	"
	Klebsiella	"

PCH = Polychlorinated hydrocarbons
PNAH = Polynuclear aromatic hydrocarbons
TOC = Total organic carbon
PCB = Polychlorinated biphenyls

*Initial values for plutonium obtained in 1978.

Source: Reference 2 of Section 2, Volume I.

3) Detailed studies during FY 1978 of alteration and other mechanisms affecting availability and release of contaminants from dredged materials after deposition.

One objective of MESA in connection with the "Expanded Water Column Characterization Cruises" (XWCC) has been to examine water quality effects such as concentrations of metals which might have been introduced by dumping. A number of attempts have been sponsored by the MESA Project in recent years to characterize the effects of ocean dumping on New York Bight sediments. Elevated concentrations of polychlorinated biphenyls (PCBs) and DDT are present in the sewage sludge dumping site in the Christiaensen Basin. Recent MESA studies have determined that there is little or no transport of PCBs from the Christiaensen Basin. Through MESA-sponsored investigations, during and prior to 1977, it has been shown that sewage sludge dumping is not the major source of contaminants in the New York Bight. MESA sponsored research also indicates that heavy metal ratios in sediments of the Bight can be indicative of the origin of metal contamination in the sediments. Other MESA studies have demonstrated that coprostanol (a hormone-like compound unique to human wastes) may represent a definitive indicator of sewage contamination in the Bight. These finding were based on comparison of coprostanol content to both polluted and relatively unpolluted areas. A further preliminary conclusion is that nearshore Bight sediments are contaminated to a degree by seawage inputs although such contamination could be due to various sources including ocean dumping of sewage sludge.

During 1977 MESA and NMFS jointly initiated the review and examination of all available information relevant to the severe oxygen depletion event off New Jersey in the summer of 1976. Preliminary results support the conclusion that dredged material dumping does not contribute significantly to such New York Bight oxygen depletion occurrences.

A.2.2.2 Spatial Sampling. The New York Bight ecosystem will be spatially sampled by subdividing into 13 segments (areas). These have been defined to "represent major areas of impact, and to approximate distinctive and often controlling bathymetric features." Sampling locations have been established to facilitate assessment of conditions and critical changes in these segments. Extensive efforts will not ordinarily be conducted in the outer continental shelf segments, which will be sampled primarily to provide controls. Transects in the nearshore area will be sampled for water quality at 1 nautical mile intervals out to approximately five nautical miles to compliment the data obtained on the more extensive seasonal sampling grid. Results of the sampling along transects may lead to modification of the experimental design of the seasonal sampling grid. Sediment sampling is to be done in both contaminated and uncontaminated strata annually. Sampling to determine contamination of shellfish will utilize standard groundfish trawl surveys of NMFS.

Data obtained at given sampling stations in field efforts may not be representative of conditions in the segments but may be atypical or extreme values. Evaluation of data point validity will rely on comparison of values with XWCC data which has been collected concurrently as part of the New York Bight Project research efforts.

A.2.2.3 Data Processing and Distribution. Sample analysis for parameters associated with concerns requiring surveillance on a bi-weekly and for some on a seasonal basis are generally to be performed and reported within 10 days of sample collection. Other parameters which are necessary to annual assessment are to be analyzed at a lower priority for data turn-around. Commercial firms are to be contracted to conduct many of these analyses. Archiving of samples, especially sediments and organisms, will enable historical data sets to be developed or re-examined in the future if needed. Arrangements are to be made with NEFC/Sandy Hook to continue their archiving facility for such samples beyond FY 1981.

A data management system will be required by the monitoring program to acquire all data produced by field efforts of the monitoring program, data available from independent research-related efforts, and from beach-related activities (which are external to the monitoring program under development by MESA). The applicable data is to be organized to expedite monitoring procedures and interpretation. Data will be "arrayed" in a manner that will facilitate updating of existing data sets with recent data. Graphical and trend-type display of data will be used although not exclusively. Monitoring program field data will probably be recorded on magnetic tape. Similar recording of data will apply to laboratory analytical results.

The monitoring program will place emphasis on intercomparability of data. Replication of sampling and analysis will be required. Coordination with other agencies and data sources will be required to assure that instrument calibration and consistent use of standards is achieved.

Data generated by other NOAA programs and non-NOAA programs will need to be incorporated into the New York Bight Monitoring Program. These data include NMFS groundfish survey results and near-shore water quality data routinely obtained by EPA Region II. Cooperative interagency agreements and formalization of data requirements are to be sought.

Timely release of results to concerned agencies and the public will follow analysis and assessment of monitoring data. In this connection, interaction with appropriate user groups is important and has been occurring. Monitoring results are being communicated to EPA Region II. In addition, the New York Bight Project is a major contributor of data and findings to the New York Bight Ad-Hoc Interagency Advisory Committee. This committee holds meetings on a monthly basis (during the April through September period) to address environmental concerns in the New York Bight such as progression of oxygen depletion, algal blooms, and evidences of degradation. Numerous Federal, state and local agencies conduct monitoring in the Bight area. Most of these are participants of the Ad-Hoc Interagency Advisory Committee and exchange data and findings. The agencies included are shown in Table A-3.

TABLE A-3

GOVERNMENTAL ENTITIES OF THE AD-HOC INTERAGENCY ADVISORY COMMITTEE

Federal

EPA Region II
Corps of Engineers, New York District
Coast Guard, Third District

Regional

Interstate Sanitation Commission

State

New York Department of Environmental Conservation
New York Department of Health
New York Department of Parks and Public Recreation
New York Department of Environmental Protection

Local

New York City DEP
New York City Health Department
Suffolk County Health Department
Nassau County Department of Public Health
Town of Hempstead

A.2.2.4 Monitoring Program Test Schedule. The testing and evaluation of the monitoring program is to be conducted in three phases. The first phase was begun in summer, 1978. The overall schedule for conducting the monitoring field test efforts is presented in Table A-4.

TABLE A-4

MONITORING PROGRAM TEST SCHEDULE
FOR THE NEW YORK BIGHT MONITORING PROJECT

			General Bight (Offshore Areas)	Near-Shore Areas
Seasonal and Annual Monitoring Field Efforts	Water Column	Dissolved Oxygen Temperature Salinity	Summer 1978	Summer 1979**
		Plankton Nutrients Turbidity	Summer 1979	Summer 1980
		Floatables Coliform	Summer 1980	Summer 1980
	Sediments	All Parameters	August 1980	August 1980
	Biota	All Parameters*	FY 1980*	FY 1980*

*Contingent upon agreement being reached with the National Marine Fisheries Service (NMFS) Northeast Fisheries Center (NEFC) for complementary work to be undertaken during groundfish surveys which are conducted fall and spring.

**Involves an agreement with the Environmental Protection Agency-Region II (EPA-RII) concerning sampling from a helicopter.

Source: Reference of Section 2, Volume I.

A.3 OCEAN PULSE PROGRAM

The Ocean Pulse Program, conducted by the Northeast Fisheries Center (NEFC), is a component of the National Marine Fisheries Service (NMFS) Fisheries Habitat Investigation Program. On the national level, the Habitat Investigation Program addresses problems of acute and chronic effects of chemical contaminants and of physical alteration of the environment on living marine resources and habitats. The Ocean Pulse Program is based substantially on existing research capabilities and environmental programs of NMFS in the Northeast. It is coordinated with activities of The NOS Ocean Dumping Program and of the NOAA/MESA Program as well as a number of public agencies such as EPA, COE, FWS, state environmental conservation departments and universities. The Ocean Pulse Program is being integrated into and is a "counterpart" of the NOAA/NMFS Marine Resource Monitoring Assessment Prediction (MARMAP) Program which predicts and assesses changes in the abundance of fishes and other living resources in continental shelf waters.

A.3.1 Program Objectives

The objective of the Ocean Pulse Program is that of solving problems in habitat protection. The program approach is to determine the status of selected fishery habitats (or strata) including estuarine, coastal and marine waters of the continental shelf adjacent to the northeastern and Mid-Atlantic states. The program will make use of traditional methods of environmental monitoring but will also emphasize "new, potentially more efficient and more sensitive methods of assessment" involving microbiology, physiology, pathology, genetics, biochemistry, etc. These methods have been emphasized by the International Council for the Exploration of the Seas (ICES) which has been working since 1975 to establish a set of standardized analytical techniques for marine pollution studies. To expedite these efforts and to fulfill its objective related to habitat protection, Ocean Pulse is to: 1) establish a system of long and short-range monitoring of the health and habitats of living marine resources, 2) develop the capability to predict the effects of habitat degradation, and 3) develop a plan for enhancement and stabilization of these habitats.

Ocean Pulse management considers that important chronic effects must be examined at the population and community levels of organization over large geographic areas where previous measurement and observation have been least satisfactory due to spatial and temporal variability. Accordingly, the Pulse Program is to be directed toward developing data baselines indicative of the current condition of fishery habitats and associated environments. Quantitative results of the program efforts are to be provided to fishery management programs such as those of the Environmental Assessment Division, National Marine Fisheries Service and other agencies which require fishery habitat information.

A.3.2 Program Description

The Northeast Fisheries Center is conducting a range of research projects (funding for these projects amounted to \$1.37 million in NOAA Base Funds and \$0.352 million in Other Agency Funding for FY 1978). These projects performed by the NEFC Oxford Laboratory, are addressing problems in pathology and environmental stress, environmental chemistry, mutagenics, biological oceanography, behavioral effects of stress on fish and coastal monitoring, assessment and protection. Some details of recent Ocean Pulse research efforts are provided in the following.

Research conducted under contract at the Osborn Laboratory of Marine Sciences in New York is investigating effects of pollution levels on parasites in key indicator fish species (winter flounders). Other research under Ocean Pulse contracts is addressing effects of PCBs on plankton size and population in order to develop monitoring tools for water column assessment. The University of New Hampshire and Southeastern Massachusetts University are establishing the baselines required for monitoring in the Gulf of Maine. An investigator at the University of Delaware has developed a monitoring baseline for heavy metals in the water column in the Gulf of Maine.

Various program products and reports are to be produced by the Ocean Pulse Program. These will include periodic status reports on research as well as finalized reports and papers specific to individual habitats (strata) addressed by the program. Data and status reports are to be processed by the Environmental Statistics Investigation in order to provide a statement of health of the particular habitat and its living resources. It is intended that results and reports be made available in a timely manner as "red flag" reports to appropriate management personnel if significant findings or problems emerge.

A.3.2.1 Measurement Program. Ocean Pulse monitoring strategy has been designed to study critical impact areas and unpolluted areas with the potential for experiencing degradation in areas such as the Gulf of Maine, Georges Bank and the Mid-Atlantic Bight. Specifically, baseline studies would address the occurrence and effects of contaminants on commercially, recreationally, and ecologically important species. Monitoring of degraded areas will examine impacts of sewage sludge dumpsites, dredge spoil dumpsites, industrial chemical dumpsites and power plant thermal effluents. Chemical and physical parameters of concern include currents, temperature, dissolved oxygen, heavy metals, pesticides and petroleum hydrocarbons. Monitoring of biotic factors is intended to reveal significant changes among indicator species in the population structure of nekton, plankton, benthos and micro-organisms essential to the food web and trophic structure of fisheries.

Some fishery habitats in the Northeast, such as the New York Bight, have been intensively investigated so that an extensive data base was available prior to the Ocean Pulse initiative; other fishery habitats have been subject to relatively little previous study. Twenty habitats have been selected by Ocean Pulse as sampling strata in the Northeast and Mid-Atlantic. Each of the strata are to be assigned internal sampling stations which will be occupied four to six times a year depending on seasonal variation, level of environmental impact and structure of communities in the stratum. During the Ocean Pulse cruises, sediment and water samples are collected for chemical analyses and bacteriological examination. Juvenile and adult fish and shellfish taken during Ocean Pulse as well as Ocean Pulse -MARMAP cruises are being examined to determine disease incidence in polluted and relatively unpolluted habitats. A significant part of Ocean Pulse assessment and monitoring efforts is done under contract.

A.3.2.2 <u>Coordination with Other Programs.</u> In cooperation with other agencies, the NOAA Ocean Pulse Program is examining the benefits of remote sensing methods. The LAMPEX (Large Area Marine Productivity Experiments) effort, designed to test the feasibility of mapping chlorophyll and total suspended solids concentration in surface waters of the continental shelf from Cape Hatteras to the Canadian border, jointly involved NASA and 21 other agencies by remote sensing from two NASA U-2 aircraft; sea-truth data were collected at 19 coastal locations between North Carolina and Maine.

Final responsibility for the Ocean Pulse Program and for intracenter coordination resides with the Director and Board of Directors of the Northeast Fisheries Center. Discipline oriented review committees are to meet twice annually to review the success of studies in obtaining data which fulfills program objectives; success of special methodologies will also be evaluated. Review committees (of from 4 to 8 members) are to be composed of Center and Regional personnel and representatives with appropriate expertise from other agencies and universities. The review committees will advise the Board of Directors and the program coordinator as to the relative level of effort which should be expended in given habitats or strata. The program coordinator has responsibility for coordinating the review committees and the principal disciplines involved in the program.

NEFC Ocean Pulse research will emphasize coastal and shelf habitats while other Federal and state agencies have responsibilities for estuarine environments; there is to be coordination of these efforts. For example, biological effects studies are being conducted at the U.S. EPA/Narragansett Bay Research Laboratory utilizing recently developed physiological measures of stress. The University of Delaware and Rutgers University have been investigating commercially important resource species and selected Delaware Bay ecosystems. Highly polluted and relatively undisturbed habitats (e.g., Newark Bay versus Little Egg Harbor) have been studied by the New Jersey Marine Sciences Consortium (NJMSC) under Sea Grant. Ocean Pulse has established that these academic groups are willing to be involved and coordinate efforts. The New Jersey Department of Environmental Protection and the New England Division COE, which are probable users of Ocean Pulse data and findings, have been consulted as to their interest in participation.

A.4 NOAA OCEAN DUMPING INVESTIGATIONS

Studies of the ecological effects of ocean dumping appear for a number of reasons within several NOAA entities.

A.4.1 Legislative Mandate

The Marine Protection, Research and Sanctuaries Act (MPRSA), enacted by Congress on October 23, 1972, was in response to concern of government and the public regarding potential adverse effects of continued unregulated ocean waste disposal. The MPRSA of 1972 includes three titles. Title I, dealing with regulatory aspects of ocean dumping, assigns regulatory authority and involvement to the EPA, the COE and to the USCG. Title II of the Act addresses research required to support the intent of the Act to limit ocean dumping of harmful materials. Section 201 of Title II assigns to the Department of Commerce, the responsiblity to initiate a program of monitoring and research to investigate the effects of ocean dumping. Research responsiblities are to be coordinated by the Department of Commerce, NOAA, in consultation with other Federal agencies. Title III of the Act, to be administered by NOAA in consultation with other Federal department and agencies, provides for designation of marine sanctuaries.

In 1975, the EPA and NOAA entered into an interagency agreement pursuant to Title II of the Act. Other Interagency agreements were initiated between NOAA and COE, and NOAA and USCG in August 1977. The interagency agreement between NOAA and COE concerns cooperative evaluations of ocean disposal of dredged materials. The interagency agreement between NOAA and USCG will establish a comprehensive program of monitoring and research for implementing Title II, Section 201 of MPRSA.

A.4.2 Ocean Dumping Program Description

NOAA's Ocean Dumping Program (ODP), initiated in FY 1977, was established to carry out a comprehensive, continuing program of research and monitoring on the effects of ocean dumping of waste materials (pursuant to Section 201 of the MPRSA). The Ocean Dumping Program is managed by the Ocean Dumping and Monitoring Division, an element of the National Ocean Survey (NOS) within the Office of Oceanic and Atmospheric Services (OAS).

The Ocean Dumping Program has no laboratories of its own; its staff is dedicated to program or project management. In FY 1978, twelve projects in the Mid- and Northeast Atlantic regions managed by ODP were performed by Woods Hole Oceanographic Institute, the Northeast Fisheries Center (NEFC), the University of Rhode Island, the Atlantic Environmental Group, and the Atlantic Oceanographic and Meterological Laboratory (AOML).

The Ocean Dumping Program is base-funded ($1.9 M in FY 1978). By pollutant category ODP allocated the following levels of base-funds in FY 1978:

Trace Metals	$309,000
Synthetic organics and pesticides	$395,800
Pathogens	$36,000
Nutrients	$172,900
Physical Alterations/Turbidity	$9,300
Uncategorized	$977,300

According to the Report and Analysis of NOAA's Ocean Pollution, Research, Development and Monitoring Activities - FY 1978 (August, 1979), no monitoring activities were identified among projects submitted in the Ocean Dumping Program inventory for FY 1978. The program emphasis was on studies of active ocean disposal, pollutant effects reseach, and the dynamics and fates of pollutants. Program data and information is used by Federal agencies including EPA, COE, USCG, and the FDA; state health and natural resource agencies; various industry groups involved with ocean dumping; environmental groups and the public.

Current emphasis of the Ocean Dumping Program is on interdisciplinary scientific research in three specific study areas in the Mid-Atlantic region and one in Puerto Rico. The Mid-Atlantic areas are:

1. The industrial waste disposal site (DWD-106) located 90 nautical miles east of Cape May, New Jersey.

2. The dredged material dumpsites in the New York Bight and the Chesapeake Bay entrance.

3. Philadelphia dumpsite (investigation of sludge dumping effects and environmental recovery).

In addition, complementary research is addressing non-site-specific chemical toxicity characteristics, toxicant-biota interactions and other questions related to oceanic waste disposal which cannot be answered by dumpsite-specific studies. The studies at Deepwater Dumpsite 106(DWD-106) represent continuations of investigations carried out since 1974. Waste dispersion, chemical interactions of waste with seawater, biological effects of waste upon fish eggs and other organisms collected at and near DWD-106, and waste toxicity to test organisms under laboratory conditions are being investigated. Acoustic studies subsequent to dumping events at DWD-106 have revealed the mechanisms affecting dispersion of waste particles. Density gradients and thermoclines have been found to prevent uniform mixing of waste with seawater such that the water forms thin layers along the density of gradients. For these reasons, waste particles remain in the upper part of the water column and should be substantially swept out of DWD-106 with water masses moving through the site. In cooperation with the Corps of Engineers, dredged material studies were initiated in 1978. The studies involve predumping investigations, experiments during dumping, and examination of cumulative effects. Dumping activities at the Philadelphia sewage sludge site are to terminate in September 1980; EPA has been studying its impacts since 1973. Beginning April 1979, NOS has been investigating ecosystem recovery of the site.

Expense precludes the conduct of numerous field expeditions (cruises) per year to obtain information requisite to such studies. Therefore, remote aerial sensing and continuous monitoring by moored and drifting arrays are increasingly attractive methods for establishing ranges of oceanic variables.

A recent article by Simpson prepared by the staff of the Ocean Dumping Program (see reference 47 of Section 2), reviews some of the technological directions that are being pursued in order to improve cost-effectiveness and augment spatial and temporal measurement capabilities. Such advances would benefit research and monitoring related and unrelated to ocean dumping.

Methods appropriate to the investigation of the dispersion of waste depend on the physical characteristics and density of the water. For example, with dredged materials which are denser than seawater, the dispersion of waste in seawater as well as its subsequent accumulation on the sea floor are investigated. Acoustic waste tracking techniques can be applied from submersible research vessels or suface research platforms. Waste that contains appreciable suspended matter (or which produces precipitates when released in seawater) can be monitored acoustically from surface vessels. Where waste plumes are not occasioned by the presence of particulates, discharged waste can be tagged with tracers (such as dyes) that enable the determination of the dispersion pattern by water sampling and remote sensing.

NASA has been involved in ocean dumping research and mapping of water quality through use of photography and multispectral scanning. Modular Multispectral Scanning (M^2S) has been used with concurrent sea-truth data in these investigations. The photographic and multispectral data enable pollution features to be located and mapped. Additionally, waste types can be identified based on their characteristic "spectral signatures". For example, based on field calibration techniques utilizing the ratio of radiance values in the pollutant plume to radiance values in the surrounding cleaner waters, acid wastes are found to have radiance peaks in the 550 to 650 nm region; the sewage sludge radiance peak is around 700 nm.

The Ocean Dumping Program plans to employ moored arrays to obtain data using sediment traps, ion exchange columns and other instrumentation. Data gathered from such moorings could be used to monitor waste dispersion and settling behavior.

Real-time tracking of waste dispersion is accomplished from ships by acoustical systems operating at 20 to 200 kHz. Particulate waste tracking is accomplished effectively by these systems. However, certain phenomena such as the deep scattering layer associated with biological activity may produce difficulties as it rises into the waste zone typically in evening hours. It is reported that differences in acoustic properties of plankton and fine-grained detritus imply that it should be possible to distinguish between waste related signals and background signals by electronic filtering. Acoustical methods have the advantage of providing continuous vertical information on waste distribution whereas fluorometric and transmissometer methods provide information only at the depth or proximity of the sensor. Improvements in the capabilties of acoustical systems are being purpused by NOAA investigators at the Atlantic Oceanographic and Meterological Laboratory (AOML) and at the Woods Hole Oceanogrpahic Institute.

Dumping provides an opportunity for investigating short-term impacts due to the intentional input of waste to the ocean as well as for drawing inferences as to the impacts of accidental inputs. However, dumping of unreasonably harmful industrial or municipal wastes is to be terminated by December 1981 such that approximately 2 years remains for such short-term impacts research. It is likely that ocean dumping research will increasingly address long-term impacts and ecosystem recovery studies.

A.4.3 Ocean Dumping Research Sponsored by Other NOAA Programs

The Ocean Dumping Program does not have exclusive responsiblity for NOAA's ocean dumping related research and monitoring. The MESA Program of the Office of Marine Pollution Assessment has been involved for several years with research and monitoring related directly and indirectly to ocean dumping. For example, approximately 60 percent of the MESA Project funding allocated for FY 1977 was applied to studying ocean dumping. Some MESA ocean dumping related studies were briefly described earlier.

A.5 NORTHEAST ATLANTIC REGION OCEAN POLLUTION MONITORING PROGRAM

The Ocean Pollution Research, Development and Monitoring Act (PL 95-273) calls on NOAA to develop an information base on present Federal programs and develop a monitoring plan. As part of the Interagency Committee on Ocean Pollution Research, Development and Monitoring, groups were organized to provide information and make recommendations called for in the legislation. One of the groups, the Subcommittee on Monitoring (SOM) recommended development and implementation of a pollution monitoring plan for the Northeast Atlantic Coastal Region based on present efforts and coordination. This recommendation has been addressed in a (May 15, 1979) draft Planning Status Report. The draft plan integrates existing and planned NOAA activities related to pollution monitoring in the Northeast Atlantic Region and provides for complete coordination with other agencies involved. The National Ocean Survey contributed to the plan by preparing an approach for monitoring in the Northeast.

The draft plan states that, in order to establish priorities in dealing with the pollution problem, the final plan would address the following questions:

- What are the pollutants in coastal waters, what is their origin, and are they increasing or decreasing?
- Is pollution localized or is it spreading in coastal waters?
- Are marine food products becoming contaminated or hazardous to man (in both the short and long-term)?

- Are marine food species stocks declining or relocating?
- Are beaches and coastal waters safe for inhabitation and recreation?
- Can degradation of ocean aesthetic quality be halted or reversed?
- Are ocean areas being degraded as living marine ecosystems regionally?
- Do pollutants and their reaction products persist in the water column and sediments and pose a long-term threat?
- Is it possible to predict future pollution and its effects on the ocean?
- What is the relationship of general disease incidence in man and animals, and increases in ocean pollution?

To address the above questions, the final plan would assemble existing information from many sources and document areas of known pollution and its effects. Additionally, it would assess the degree of pollutant stress in the areas and the cause and effect relationship between activities, events and pollution. Analyses of these findings are to provide a priority list of geographic areas for monitoring.

A.5.1 Program Objectives

The Northeast Atlantic Coast Pollution Monitoring Program has two goals:

- Maintain an assessment of the health of the regional marine ecosystem.
- Provide the necessary information to ensure present and future protection of human health and the marine ecosystem and to carry out wise management of marine resources of the region.

During the first 2 or 3 years of the program, monitoring would be conducted for 24 sites and 8 tracks at selected impact areas, unstressed (control) areas, and critical habitats in the Northeast and Mid-Atlantic coastal waters. Measurements and sampling by the ongoing NOAA monitoring programs will be specifically determined by those existing programs and incorporated into the Northeast Atlantic Coast Pollution Monitoring Program.

The draft plan notes that pursuant to the above program goals, it will be necessary to develop operational sampling systems with quality control of measurement data. In addition it would be necessary to develop international reference standards and measurement techniques ensuring highest quality physical, chemical and biological analyses of the water column, sediments and fish species. It will be necessary to determine levels of petroleum compounds, heavy metals, halogenated hydrocarbons, domestic waste contaminants, and radioactive isotopes in selected species at 16 of the 24 monitoring network sites in samples collected four times per year. Water column analyses would measure these same contaminants plus suspended solids at various depths at the stations four times a year. For sediments, the above pollutants, populations of organisms, and seabed oxygen consumption would be measured at 10 of the 24 monitoring network stations four times a year. Phytoplankton dynamics would be determined at 10 of the 24 stations four times a year. Current direction, speed, salinity, dissolved oxygen and turbidity would be determined at selected depths along with meteorological conditions would be determined at 5 sites continuously and at 19 sites four times a year.

Baselines would be constructed from the monitoring data. Correlation of measurements of parameters in compartments of the environment would be evaluated. Long and short-term variation of parameters at each monitoring network site would be determined. The site measurement data and implications of biological research and investigation would provide warnings of critical conditions, hazards, and impacted ocean areas to appropriate agencies and authorities. Through cooperation with research groups, models of water movements, fish species behavior, fish species population, and pollution dynamics at and contiguous to site areas would be developed. Measured and interpreted data would be provided to research groups with responsibilities to determine sources, fates and effects of pollutants.

The program would have specific outputs which could include an annual atlas, monthly reports on significant anomalies, crisis reports with appropriate frequency, contaminant levels and variations, circulation patterns (monthly), assessment reports by principal investigators, short-term and long-term trend analyses, and annual administrative reports of progress.

The preparation of a Program Development Plan for the Northeast Atlantic Region Monitoring Program was approved by the Deputy Administrator of NOAA on September 27, 1979. The program is to begin by January 1, 1980, and will be managed by National Marine Fisheries (NMFS) personnel. The significance of the National Ocean Survey (NOS) monitoring plan remains to be seen. Those responsible for developing the monitoring program were contacted anyway because of the effort they had invested in developing a rational approach to an observation program in the Mid-Atlantic Bight.

A.5.2 Pilot Monitoring Project

The first phase of the monitoring program envisioned by NOS for the Northeast Atlantic Region would be a Pilot Monitoring Project developed around the monitoring activities of the ongoing NOAA marine environmental programs in the area. The Pilot Monitoring Plan would be based on portions of the Northeast Atlantic Region Monitoring Plan.

APPENDIX B

EMERGING TECHNOLOGY FOR LABORATORY AND *IN SITU* MARINE POLLUTION MEASUREMENT

B.1 INTRODUCTION

This Appendix identifies recent advances in the laboratory and *in situ* measurement technology for marine pollution. In Chapter 5 some of the significant development areas and directions in the emerging technology for laboratory and *in situ* marine pollution measurement are examined in relation to technical needs derived for NOAAs programs. The discussion in Chapter 5 is based substantially on information assembled in a search of recent literature sources which is presented in the following.

B.2 EMERGING INSTRUMENTATION

Recent developments in instrumentation for laboratory and *in situ* measurement of chemical substances (including pollutants) and oceanographic parameters are of several kinds. Significant developments include the emergence of instruments or systems which are *new* from an engineering standpoint, the trend toward the greater utilization or acceptance of one of several competing instrumental methods, and the adaptation of *existing* instrumentation for applications which are advantageous in marine pollution work. The latter can include the development of automated as well as portable versions of an instrument and modification for use in field, remote or shipboard measurement. Some recent developments fulfill several of these criteria.

B.2.1 Emerging Laboratory Instrumentation

Although the discussion of conventional laboratory instrumentation presented in Section 4 centers on instrumental methods which are well established and longstanding, trends in instrument development may result in the significant advantage of one over another. In this evolutionary sense, conventional and emerging technology may be indistinguishable and the designation of a technology as conventional or emerging becomes somewhat arbitrary. For example, high-pressure (also called high-performance) liquid chromatography (HPLC) is a longstanding technique in principle. However, its history has not been one of steady growth since its inception. Rather HPLC has undergone a sudden strong growth in application over the last few years, and is considered to be an emerging technology.

B.2.1.1 Chromatography. Among the numerous chromatographic techniques which include gas chromatography, liquid chromatography, thin-layer chromatography, HPLC, a variant of liquid chromatography, is exhibiting the greatest growth according to Robinson.(1) The variety of liquid chromatographic techniques all rely on use of a narrow column packed with a material which restricts flow of the components of a sample dissolved in a liquid (mobile) phase passing through the column. One of the former disadvantages of liquid chromatography which impeded its growth was that the process was time-consuming. However, the rate at which separations can be accomplished has been increased considerably by use of small packing particles (typically spheres in the 5 to 10 micron range) in columns only 10 to 25 cm in length. Consequently, travel distances and times in the column are considerably reduced. However, this requires application of pressures in the range of 1000 to 5000 psi to the liquid phase and requires special pumps capable of providing a constant flow.

Various forms of HPLC are distinguishable based on the type of affinity between the packing material and the components of the sample. Consequently, adsorption chromatography utilizes porous solid materials such as silica gel with a high ratio of surface area to volume. HPLC which relies on differential solubility of components in a liquid present as a coating on the stationary phase is called partition chromatography. Ion exchange chromatography utilizes ion exchange resins in the form of small or porous particles to serve as the column packing material. Size exclusion chromatography utilizes packing materials with pore sizes small enough to physically separate molecules depending on their dimensions. The ion exclusion technique is primarily used for polymer analyses (e.g., molecular weight determinations).

Proponents of HPLC point out that it is probably the most versatile chromatographic technique, permitting analysis of 80 to 85 percent of all compounds.

Gas chromatography relies upon the ability to generate a vaporized sample without degrading or decomposing its molecular components, so it is limited to the analysis of relatively volatile compounds and is more successful with those of low molecular weight (less than 200). Accordingly, gas chromatography is most effective with compounds having molecular weight less than 200. In contrast, HPLC is applicable to the analysis of compounds with molecular weight in the range of 100 through several million.

Several detector types are available in HPLC systems. The most common detectors in use are based on measurement of optical properties such as refractive index, ultraviolet absorption, or fluorescence emission. The refractive index detector offers the most versatility but is less sensitive than other detectors.

Many current HPLC instruments are oriented toward testing large numbers of samples with the minimum of operator attention. Microcomputers have had an important role in the emergency of HPLC from the standpoint of both system operation and control as well as output data processing. For example, in the routine analysis of multicomponent samples with HPLC, the optimum mobile phase solvent would yield peak separations in the output that would be sufficient to resolve peaks but would not be too widely spaced thereby sacrificing analytical speed. By continuously varying the composition of the mobile phase solvent during chromatograph operation, peak positions (retention times) can be manipulated. In HPLCs with this capability, the microcomputer could be programmed to execute the appropriate control of mobile phase composition. As in other forms of chromatography, peak positions (and hence retention times) are the basis of sample constituent indentification; peak areas are related to the amount of each component present. HPLC associated data systems report the elution times and peak areas, and, often, are available with options to perform mathematical or statistical analysis of output data and chromatograms.

Cost of HPLC instruments ranges up to approximately $40K for top-of-the-line laboratory instruments. Systems for unattended, industrial quality control applications where diverse analytical options are not needed are available in the $4K to $8K range. This may be indicative of the economics which could be achieved with HPLCs amenable to unattended, in situ applications. Technicon Industrial Systems and other manufacturers are developing automated sample preparation systems for HPLCs. The Technicon FAST-LC system can automatically perform solvent extraction, filtering, derivatization, and evaporation steps with samples prior to injection into the HPLC. As in other areas of chromatography, combinations of instrumental techniques are an important trend in HPLC. Accordingly, HPLC instrument combinations with mass spectrometers (HPLC/MS), or with infrared spectrophotometers are currently becoming available.

B.2.1.2 Automation. The Lawrence Livermore Laboratory (LLL) and the U.S. Environmental Protection Agency jointly conducted a project as reported by Taber et al.(2) to develop instrument calls and real-time code for laboratory automation. The resulting programs are intended to provide an "interface between the analytical instruments and the BASIC language programs for data reduction and analysis." Laboratory instruments automated in this way include Technicon Auto Analyzers, atomic absorption spectrophotometers, total organic carbon analyzers, an emission spectrometer, an electronic balance, sample chargers and an optical spectrophotometer. A report of the Lawrence Livermore Laboratory by Crawford(3) describes a program (TAINN computer program) developed for automating the Technicon AutoAnalyzer for trace constituent analysis of water.

Rigdon et al.[4] at Lawrence Livermore Laboratory (LLL) have designed a computer automation system for a total organic carbon (TOC) analyzer. The automation system was designed for use with the Beckman Model 915 TOC analyzer. The programs execute on a Data General NOVA-840 computer operating on multi-user BASIC language. The automation system could also operate with similar carbon analyzers and other software systems following appropriate changes.

B.2.1.3 Other Developments. Hoover and Long[5] described a prototype instrument for determination of phosphorus in water. The instrument is a second-generation flame spectrometer providing linear response to phosphorus in the form of phosphoric acid in the 0.5 to 16 ppm range and is reported to exhibit a 20 percent analytical standard deviation in this range. Analyses of higher range EPA Nutrient Reference Samples (approximately 0.5 ppm phosphorus) were in agreement with the reference values (within one standard deviation) for both inorganic and organic phosphorus.

A continously operating total organic carbon (TOC) analyzer has been described[6] which incorporates low-temperature (60 deg. C), high intensity UV promoted chemical oxidation instead of conventional pyrolysis at high temperature. Elimination of the hot reaction furnace reduces the possibility of explosion as well as eliminating time-consuming shutdown and exchange due to frequent high-temperature reactor failure. During operation, water to be analyzed is continuously pumped into the instrument and is combined with a phosphate-acid flow. The combined flow passes through an inorganic C-removal sparger and gas-liquid separator. The (carbonate-free) flow is then combined with a persulfate flow and is passed through a quartz reaction coil where the organic carbon is oxidized to CO_2 in the presence of UV light. The resulting CO_2 is then transferred to the gas phase which is conducted to a CO_2-specific IR detector.

Veith and Kiwus(7) report development of a modified Nielsen-Kryger steam-distillation apparatus capable of exhaustive distillation of pesticides and industrial chemicals from water, sediment, or tissue samples with subsequent extraction of the distillate with an organic solvent. The extract can generally be analyzed directly with gas-liquid chromatographic instruments averting the need for concentration and cleanup procedures.

B.2.2 Emerging In Situ and Field Measurement Method

Numerous recent research and development efforts have resulted in the refinement or adaptation of existing technology for the measurement of pollutants and of oceanographic parameters in the field. Several examples of such instrumentation are for the measurement of organic pollutants in the field. Gummage et al.(8) provide a survey of new instruments and techniques for monitoring synfuel pollutants including polynuclear aromatic hydrocarbons and for analysis of phenols and thiocyanate in wastewater. Instrumental methods discussed include second derivative UV absorption, synchronous luminescence, photoacoustic spectrometries, room temperature phosphorescence, a portable mass spectrometric technique, differential sublimation, and thermoluminescence.

Goodson et al.(9) report results with a Cholinesterase Antagonist Monitor (CAM-1) to sense the presence of low concentations of cholinesterase inhibitors in water in real-time mode. Laboratory tests with the instrument demonstrated its ability to detect subtoxic levels of 22 organosphosphate and 7 carbamate pesticides. Goodson et al.(10) have designed and tested a portable instrument which is a field version of the laboratory cholinesterase monitor. The authors report that the system can be run with portable power supplies (e.g., a 12 volt battery) by one operator and is sufficiently compact for convenient ship-board use.

Badley and Heaton(11) described a portable analytical system for determination of trace volatile pollutants in water. The system includes a small gas chromatograph coupled to a commercial volatile organics analyzer (VOA). The system was constructed with support components including an H_2 generator, air and N_2 cylinders and regulators. The system operates with either direct injection into the gas chromatograph or with preconcentration of organics by N_2 sparging of the water samples and absorption on polymer with subsequent desorption and determination by GC. Concentrations of 0.01

ppm of acrolein, allyl chloride, epichlorohydrin, vinyl chloride, 1-2-dichloroethane, and benzene as representative compounds were detectable in 5 ml water samples with preconcentration.

Marinenko(12) developed an apparatus for monitoring dissolved chlorine concentration in water. The apparatus is the subject of a U.S. patent; it claims a high sensitivity and advantages in calibration capability. Following mixing of the water sample with a potassium iodide solution, the resulting solution is transferred to a detection-calibration assembly where iodine (resulting from oxidation of iodine upon conversion of Cl_2 to chloride) is detected amperometrically. Calibration is accomplished by means of an upstream calibration cell which supplies iodine at known levels to the detection cell.

Capabilities and operating characteristics of three types of microbiological detection systems for water are described by Jeffers and Taylor.(13) A continuous flow chemiluminescence sensor detects total bacteria by measuring light emitted when porphyrins catalyze a luminol-hydrogen peroxide reaction. A bioluminescence sensor detects ATP in living cells by measuring light emitted in a biochemical process. An electrochemical sensor detects coliforms, either total or fecal, by measuring the H_2 produced by metabolism.

The Pye Unicam Automatic Water Analysis System (manufactured by Pye Unicam Ltd., Cambridge, England) has been described by

Cottrell.(14) The system automatically performs sample dilution, reagent addition, mixing, incubation, and transfer of the processed sample to a single-beam grating spectrophotometer for measurement. A range of water analysis methods has been performed with the system. These include analysis for ammonia, silicate, phosphate, COD, nitrate, nitrite, alkalinity, and hydrazine. The author claims that the system is cheaper and faster than other comparable automatic analyzers and has better analytical output from a cost-benefit standpoint than does a continuous flow (three-channel) system under optimum operating conditions.

Peck et al.(15) automated a commercial inductively-coupled plasma spectrometer to permit unattended operation and data collection. The authors discuss the analysis of natural water samples with the system. Automation is achieved by using a microcomputer permitting interconnection of a sample changer, card reader, high-speed printer terminal, a dual floppy disk drive, and the spectrometer's basic computer.

Work underway at the National Ocean Survey, Engineering Development Laboratory of the National Oceanic and Atmospheric Administration, is addressing the development and testing of an operational engineering model of an underway towed system for heavy metal measurements at ocean dumpsites.(16) A design concept study of the system has resulted in system specifications and a work statement for its development. Review of the project by the NOAA Dumpsite Monitoring Office is in progress.

A prototype, helicopter-borne, water quality monitoring system has been developed and evaluated as reported by Wallace et al.(17) Helicopter test flights with the system were conducted to survey an area of the James River, Va., in the vicinity of nuclear power plant cooling water discharges. The system is lightweight, utilizes commercially available sensors for immediate readout, and can obtain samples for laboratory analysis. The system described is specifically for rapidly assessing hazardous material spills in coastal waters and was designed with temperature, conductivity, pH and dissolved oxygen measuring capabilities; measurement capabilities could be readily expanded.

Argonne National Laboratory has developed instrumentation and techniques for measuring three-dimensional temperature structure of thermal plumes (from power plants), along with the limnological, meteorological, and plant operating conditions affecting plume behavior.(18) Plume mapping is accomplished by coordinating the instantaneous location of the boat transporting the apparatus, together with subsurface temperature measurements from a towed thermistor chain to produce a quasi-synoptic view of plume structure. Real-time, onboard display of vertical temperature measurements enables operators to determine the extent and spatial resolution of measurement required. Design, reliability, accuracy, calibration information are provided for system components. Supportive studies are described which address plume dynamics, eddy diffusivities, and time-temperature histories of water parcels in thermal plumes.

B.2.3 Emerging Technology for In Situ Petroleum Pollution Monitoring

Petroleum pollution is exceedingly complex so that comprehensive monitoring must address the impact of numerous petroleum-related compounds in various compartments of the environment in both the long and short term. In view of the increased emphasis accorded to petroleum-related pollutant monitoring as well as the variety of instrumentation which has been developed in recent years, a separate discussion of in situ petroleum pollution instrumentation is presented.

Although the Northeast Atlantic coastal and offshore environment has been subject to inputs of petroleum and its synthetic derivatives as a consequence of intensive industrialization, maritime shipping, tankering operations and other sources, concern for the impacts of petroleum inputs in the Mid- and North-Atlantic region has been heightened by the initiation of outer continental shelf (OCS) oil and gas exploration in the Baltimore Canyon area as well as the likelihood of similar activities in the Georges Bank area. In addition, the Argo Merchant oil spill incident (December 1976 off Nantucket, Massachusetts) has intensified regional concern over oil pollution even though the spill did not reach the coastline.

Oil and grease include naturally produced fat-soluble compounds, a diverse range of petroleum derivatives, as well as various synthetic organic compounds.(19) Crude oils may contain many thousands of compounds and consist principally of hydrocarbons and their derivatives with appreciable combined sulfur, nitrogen and relatively less oxygen as well as low concentrations of metals including nickel, vanadium and iron complexed by natural organic chelates. Crude oils contain three general classes of hydrocarbons; these are the alkanes, cycloalkanes, and aromatics (but not alkene hydrocarbons). The normal alkanes ranging from methane to beyond C_{60} are present with essentially equal abundance of the even and the odd numbered carbon chains. A complex mixture of five and six-carbon, saturated ring structures is present in crude oils. Aromatics include six-carbon unsaturated ring structures (e.g., benzene). The aromatics also include complex mixtures of mono-, di-, tri-, and tetraalkyl benzenes, naphthalenes, and polynuclear aromatic hydrocarbons with multiple alkyl substitutions. Hydrocarbons from refined products as well as crude oil consist of diverse mixtures of classes covering a range of volatility. These substances exhibit considerable diversity in their solubility and other chemical properties, persistence in the environment, and toxicity.

In recent years, extensive research has been devoted to development of oil-water separators. This has been necessitated by federal regulations which require that discharge of bilge and ballast water cannot violate water quality standards. In addition, effluent discharged from onshore refineries utilizing gravity separator/dissolved air flotation typically contains about 20 parts per million of dispersed oil. Process changes are being implemented by refineries to minimize these discharges and there is strong pressure to reduce oil content to beneath 20 parts per million. The development of improved separator technology has emphasized the need to continuously monitor the concentration of oil in the water.

A variety of analytical requirements is related to oil in the environment. Determination of total oil in the water column and sediments, fractions of different volatility, alkane and aromatic components, and individual molecular species of oils might be required. A variety of laboratory methods and instrumentation is available to determine these parameters (see Appendix C on petroleum hydrocarbon analysis and Section 4.2 which discusses principal laboratory instrumentation for analysis of organic substances).

Various systems have been developed and tested for continuous, in situ monitoring of oil in water. These have been based on measurement of total organic carbon (TOC), infrared absorption, fluorescence, optical scattering, gas chromatography, and simulated distillation of oil products. Tyler et al.(20) showed that a carbon analyzer could be utilized for this monitoring application. A system was designed based on the Beckman 915 Total Organic Carbon Analyzer. This system was modified in order to simultaneously process a total carbon sample and an inorganic sample. Readings from two analyzers are simultaneously processed by analog modules to compensate and subtract the readings; the resulting signal, corresponding to organic carbon content, is recorded on a strip chart. The system developed by Tyler et al. permits rapid analyses of oil in water having an operational turnaround time of 55 seconds. The system is capable of measuring the concentrations of any type of organic oil in water in the range of 1 to 50 parts per million employing only one calibration curve.

Ricci and Kelly(21) reported the development of a multiphased dye transfer methodology for monitoring oil in water over the range of 1 through 200 parts per million. The technique offers a low-cost, reliable instrument of small physical size which provides accuracy even in the presence of solids, detergents and other contaminants as well as applicability to virtually any oil type. Ricci and Kelly report that the process can serve as a basis for portable, semiautomatic systems for field or shipboard use; and fully automatic continuous monitoring remote systems capable of telemetering information of contamination levels.

Light-scattering measurement techniques are the basis of several existing or proposed instrumental systems for monitoring oil in waters. Friedman(22) assessed the potential of measuring angular-intensity distribution of scattered light for discriminating between oil and particulates. It was concluded that, under actual field conditions, distinguishing oil from particulates by use of angular-intensity distribution of scattered light alone would be difficult. However, Batutis and Skewes(23) developed a shipboard oil-in-water monitoring approach based on forward (laser) light-scattering techniques. The authors claim that the concept has the capacity to detect a wide variety of oils in the 0 through 100 parts per million concentration range with rapid measurement rates (approximately 10 seconds per measurement). Furthermore, the response was found to be linear and reproducible or amenable to compensation despite the presence of possible interfering agents and variety of operating circumstances tested. These included effects of dirt and detergent, oil droplet size, varied salinities and temperatures.

P.R. Mallory and Co. report(24) the development of a prototype instrument which can detect escaping hydrocarbons in areas where this was not formerly possible or practical. The device relies on a sensor which detects the pressure of oil, gasoline or other hydrocarbons in thin pollution layers on the water surface. The sensor measures differences in thermal conductivity between hydrocarbons and water and could find application in monitoring leaks in storage tanks, tankers, petroleum exploration and drilling-related leaks, and in environmental monitoring applications.

Goodson, et al.(25) reported the development of a low cost, rapid detection system that would be sensitive to the presence of small quantities of oil and could be deployed on buoys for use in local area pollution surveillance systems. The system relies on two Taguchi Gas Sensors (semiconductor, stannic oxide on a support) which respond to hydrocarbon vapors or carbon monoxide. Covering one of the sensors with a semipermeable membrane permits it to respond to carbon monoxide and prevents its response to hydrocarbon vapors such that the pair of sensors in parallel can distinguish exhaust gases from oil spilled or released to the water.

A continuous sampling water analyzer has been described(26) recently which provides rapid response and low cost detection of hydrocarbon spills in the 0 to 10 parts per million range. The system employs a hydrogen flame ionization detector and a 2-phase (gas-liquid) extractor to detect impurities in water serving to indicate hydrocarbon spill or release. The system transfers impurities from a continuously flowing water sample into a nitrogen decarrier gas phase which conveys these into the flame ionization detector. Response time to change in concentration levels of selected indicator impurities is on the order of 30 sec.

While the systems described above enable sensitive detection of oil or hydrocarbons on water and others permit measurement of total oil in water samples, the real-time, in situ measurement of petroleum components is possible and is being pursued. Hiltabrand(27) reports that the USCG Research and Development Center began the testing of an ENDECO towed underwater fluorometer system in March 1978 to measure instrument performance and determine background aromatic hydrocarbons in the water column at the deepwater port site Louisiana Offshore Oil Port, Inc. Oil concentration, temperature, turbidity, and depth were monitored continuously during the experiment. Oil concentrations determined were in the 30 to 300 parts per billion range.

Although petroleum hydrocarbons can be separated into three major classes, paraffins, cycloalkanes and aromatics, only the aromatics contain compounds that were designated as toxic substances requiring priority attention by the U.S. Environmental Protection Agency (1975, as cited in Chemical Pollutants of the New York Bight; Priorities for Research, NOAA, 1979).(28) The polynuclear aromatic hydrocarbons (PNAHs) including benzanthracene, naphthalene, benzene, benzofluoranthene, benzopyrene, chrysenes, dibenzanthracenes, ethyl benzene, and toluene have been shown to be carcinogenic and are suspected as being neoplastogenic. However, aromatic hydrocarbons present in the environment are not exclusively the result of petroleum pollution. Aromatic hydrocarbons have been isolated from terrestrial plants and polynuclear aromatic hydrocarbons may be synthesized by marine microorganisms. In any event, the widespread occurrence of polynuclear aromatic hydrocarbons in the marine environment suggests that they may be synthesized by plants and microorganisms. The difficulty of distinguishing petroleum hydrocarbons from biogenic hydrocarbons in sediments, organisms and water is part of the larger problem of understanding and predicting the fates and transfers of petroleum hydrocarbons in the marine environment so that further research is needed in order to provide definitive tests for petroleum pollution and its impact. In view of the chemical complexity of petroleum and its derivatives, and the fact that monitoring related to oil pollution may require measurement of numerous parameters in different compartments of the environment utilizing a variety of instrumentation, there is considerable difficulty of intercomparability of measurements and findings. Therefore, the standarization of analytical methods and instrumentation in the laboratory and the field should be pursued. In addition, definitive parameters need to be specified and uniform analytical protocols adopted.

B.3 EMERGING ANALYTICAL METHODS

This section examines recent developments in analytical methodology relevant to the measurement of marine pollution. Standard analytical methods of analysis are presented in Appendix C. In view of the fact that emerging methods described in the technical literature are often not reported explicity as laboratory or in situ techniques as well as the fact that many laboratory analytical techniques can be adapted for field use (and vice versa), this section does not make a distinction between laboratory and in situ methods in each case. However, where it has been reported that a method has been applied for in situ measurement such will be indicated.

B.3.1 Analytical Methodology

The organohalogens including various pesticides, PCBs, DDT, pentachlorophenol, trifluralin and numerous other compounds continue to receive priority as environmental concerns and are targeted pollutants addressed by many environmental monitoring programs. A recent literature review of Chian et al.(29) presents extensive data on instrumental methods and their capabilities in the analysis of numerous compounds in this class. The information was derived from results of many recent independent studies; an extensive listing of bibliographic sources is provided. Improvements in analytical capabilities have been occurring rapidly due to efforts of many researchers developing new methods of sample pretreatment and selective extraction procedures in conjunction with gas chromatographic (and

GC/MS) techniques. Other separation and detection techniques use NMR, HPLC, and pulse polarography. HPLC as a general instrument method was discussed earlier in this Appendix. Several recent articles describing new methods and techniques of analysis of these compounds are summarized in the following.

Rensburg et al.(30) have reported a semi-automatic method which is claimed to offer rapid, sensitive, economic analysis capability for volatile organohalogens in water. The method is based on a rapid liquid-liquid extraction process and gas chromatographic analysis with electron capture detection. A linear analytical range is obtained for many organohalogen compounds in the range from 0.3 to 300 ppb.

Deitz and Singley(31) compared four different sample handling techniques for the gas chromatographic analysis of volatile chlorinated hydrocarbons. The techniques were direct aqueous injection, solvent extraction, gas stripping, and static headspace sampling. The objective of the study was to select a routine method to be applied in analysis of drinking water, natural water, and industrial effluents containing volatile organohalogens such as chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), trichlorethylene (C_2HCl_3), and tetrachloroethylene (C_2Cl_4). The method sought was one which would not be adversely affected by less volatile chlorinated and non-chlorinated compounds. Gas-stripping techniques are time-consuming where routine application to a large number of samples is required. Furthermore, with direct aqueous injection and solvent extraction procedures, interference due to compounds not of interest cannot be prevented. The authors found that the headspace method was preferable to purge-trap methods that are in wide use currently for routine sample analysis for volatile chlorinated hydrocarbons. The static headspace method is based on the fact that an aqueous sample containing organic compounds, if sealed in a vial, undergoes partitioning (or equilibration) between the water and the vapor phase with the more volatile, water-soluble organics being more strongly partitioned into the vapor. Applying the static-headspace sample handling technique in analysis for the chlorinated hydrocarbons listed above in the 0.1 to 30 ppb range, Deitz and Singley reported a precision of approximately 3%.

An analytical methodology for determining Kepone in water and sediments is described by Lee and Saleh.(32) The method adapts the regular, multiresidue procedure for the common hydrocarbon pesticides and PCBs from the Florisil column. Kepone is eluted with 200 ml of a 10% methanol/5% benzene mixture, in hexane. The lower detection limit cited for Kepone in water is 20 ng/liter.

The complexity of trace element analysis of environmental samples is increasing as it is recognized that the simple determination of total metals is not sufficient but that metals speciation and chemical availability must be determined or monitored. In addition, the fates and transfers of most pollutants including metals are receiving increased attention for all compartments of the environment including the water column. The significance of trace metal pollution in sediments and in biota are discussed in Section 5.1 and Appendix B subsequently. In the following, new or improved methods reported in recent literature are discussed. Many are applicable to analysis of water although trace element analytical methodology can often be adapted to sediment or biological samples depending on extraction procedures or the exact parameter to be measured (for example, total metals versus adsorbed metals in sediments). Standard methods of trace metal analysis of natural waters are described in Appendix C; principal laboratory instrumentation for trace element analysis has been discussed in Section 4.1.

Davis et al.(33) have described a method utilizing high-speed anodic stripping voltammetry in determining total arsenic at the nanogram level. The arsenic present in samples is converted to arsenic chloride by treatment with a combination of hydrochloric acid and cuprous chloride subsequent to wet ashing with a mixture of nitric, perchloric, and sulfuric acids. The arsenic trichloride is volatilized and collected in 4 ml of deionized water yielding a solution which is then analyzed for its arsenic content by voltammetry. The authors claim a precision with relative standard deviation of 7% at the 50 nanogram level of arsenic; analysis time is reported to be about 140 sec per sample.

Whetter and Ulrey(34) report an improved fluorometric method for determining selenium. The authors modified a previously reported method of analysis of biological materials for selenium with a claimed reduction of equipment and labor requirements. The procedure involves sample digestion, neutralization, chelation with EDTA, complexing with 2,3-diaminonaphthalene, and extraction of the piazoselenol into cyclohexane. The cyclohexane is then transferred to fluorometer tubes for analysis. As many as 10 determinations can be performed per hour; a standard error of determination of approximately 7 percent is reported.

Pyen and Fishman(35) have described an autoanalyzer method for determination of selenium in water. The method employs sodium borhydride ($NaHB_4$) rather than Al slurry to convert inorganic selenium to its hydride; an atomic absorption spectrometer equipped with an electrodeless Se discharge lamp was used. Automated equipment included a Technicon sampler, proportioning pump, heating bath, stripping column, and tube furnace. The method is reported to enable analysis of water and water-suspended sediment mixtures with as little as 0.1 ppb selenium.

A method for determination of cadmium, lead and copper in water employing anodic stripping voltammetry has been described by Howe and Jones.(36) The Tennessee Valley Authority developed the method for determining total concentrations of cadmium and lead in water samples. Following digestion of the sample and addition of reagents to overcome interferences for iron (III) and selenium (IV), peak current for cadmium and lead is measured and quantified by standardization. The analytical range reported for the method is 0.3 to 100 ppb of cadmium and 30 to 100 ppb of lead. Limited data have indicated that the method can probably be used for determination of copper in the 5 to 100 ppb range but is unsuitable for zinc.

A procedure reported by Fitzgerald(37) offers the capability to detect mercury in environmental samples at the parts per trillion level. The method involves a cold-trap preconcentration with subsequent flameless atomic absorption analysis of mercury. The method has been used in laboratory and shipboard analysis of mercury in seawater. A detection limit of about 0.2 parts per trillion for mercury is reported; for seawater containing 25 parts per trillion of mercury, the coefficient of variation was reported to be approximately 15 percent.

Trace metals occur in seawater and marine sediments in a range of chemical forms and species. Organometallic species arise from the organic complexation and chelation of metals as well as the formation of stable organometallic compounds. These mechanisms may considerably enhance the solubility of metals as compared with purely inorganic metal speciation and are important factors influencing metals transport and transfer in the marine environment. In addition, certain trace metal pollutants in the marine environment such as mercury, lead, arsenic, and selenium may be converted due to microbial agents to various methylated and other organic molecular forms. The resulting compounds present a greater environmental hazard due to their higher toxicity and enhanced mobility than do the inorganic species. Accordingly, analytical methodology for investigating and determining organometallic substances continues to receive emphasis in current literature.

Van Loon(38) has discussed techniques for investigating and determining organometallics utilizing combined chromatographic and atomic spectrometric instrumentation. As noted by Van Loon, investigation of metals speciation has been a particularly challenging area. Until recently most work in this area has employed electrochemical or chromatographic techniques utilizing conventional detectors. Interpretation of results is often difficult, subtle, and time-consuming with the aforementioned methods such that research on metal speciation problems has progressed rather slowly. Relatively little use has been made of atomic absorption, emission, and fluorescence spectrometers as detectors in metal speciation studies involving chromatography. However, the metals specific nature of these detectors overcomes the complexity and much of the subjectivity of metals speciation studies permitting economically feasible, routine accumulation of speciation data. Several studies have employed combined chromatographic-atomic absorption instrumentation in metals speciation work. Van Loon et al.(39) were first to propose use of an atomic fluorescence spectrometer as a detector in metals speciation-chromatographic studies. Little use has been made to date of atomic fluorescence detectors in metal speciation work although this technique would provide simultaneous multielement capability. In fact, no commercial atomic fluorescence equipment exists at present. The atomic absorption spectrometer would be the most likely detector for most laboratories since it is widely available and subject to relatively few spectral interference problems as compared with emission spectrometry.

Van Loon(38) also discusses techniques for interfacing atomic spectroscopic with chromatographic systems. Nebulizer performance is an important factor although chromatographic (mobile phase) flow rate can be considerably lower than typical nebulizer flow rates without substantially reducing atomic absorption signal levels. Chromatographic flow rate can be supplemented by providing an auxiliary solvent flow in order to match the nebulizer flow rate.

Combined chromatography-atomic absorption spectroscopy has been applied to investigations of biomethylation of Hg, Se, and Pb. In addition, mercury compounds have been studied in fish, arsenic compounds analyzed in water, selenium compounds measured in plant transpiration gases, chromium in its carcinogenic hexavalent forms has been determined in natural waters, and copper chelates of NTA, EDTA, EGTA, and CDTA have been separated and determined.

In a recent study, Simon et al.(40) reviewed methods for the sensitive determination of organometallic compounds of copper, mercury, and tin in water. Their report describes methods of extracting and concentrating these compounds prior to determination by atomic absorption spectrometry. A gas chromatographic method for determining organometallic compounds without requiring extraction or preconcentration steps is also described. A hydrogen-rich, flame ionization detector which offers sensitivity and selectivity in the lower nanogram ranges was developed.

MacCrehan and Durst(41) have developed a method for measurement of organomercury cations employing liquid chromatography with differential pulse electrochemical detection. Considerations related to optimization of reductive electrochemical measurement in consequence of apparatus design are discussed. A high degree of selectivity is achievable with the differential pulse mode of detection and has been demonstrated by the authors. The development of a charge-neutralization, reverse phase separation of methyl-, ethyl-, and phenylmercury cations is discussed. A detection limit of 2 ppb is claimed for methylmercury. The method was applied by the authors in the analysis of biological materials. These included tuna and shark tissue samples.

Several recent articles have described new methods for the determination of nitrogen compounds and species in natural waters. McClean et al.(42) describe a polarographic method for the detection of ammonia and amines as low as 25 ppb in brine samples based on their reaction with excess formaldehyde. Ion-exchange treatment of the formaldehyde reagent was employed to minimize blank problems. Nitrate and nitrite was determined polarographically based on the catalytic effect of uranyl ions. Total nitrogen as determined by a combination of these methods compared favorably with results obtained with more conventional methods. The authors report that a differential pulse polarographic instrument or recently developed digital analyzer can be used for the method they describe.

Berg and Abdullah(43) have described a method for determination of ammonia in seawater and estuarine water utilizing an autoanalyzer. They report that ammonia in water is determinable by their method in the concentration range of 0.2 to 20 mg ammonia N/liter over a 10 to 35 parts per thousand salinity range; interferences due to amino acids were found to be negligible.

A method for the shipboard measurement of dissolved nitrous oxide (N_2O) in seawater has been developed as reported by

Cohen.(44) The method involves stripping nitrous oxide from solution, absorption by molecular sieve, and subsequent analysis by gas chromatography with electron capture detection. A precision of 2% is claimed and an overall accuracy of 3% reported. The nitrous oxide distribution of Pacific tropical waters was investigated utilizing the method.

An ongoing research program is being conducted by the Naval Research Laboratory(45) to develop and utilize shipboard and *in situ* methods of measuring concentration of gases in the ocean and atmosphere with the objectives of improved pollution assessment in the marine environment, determining the relationships of dissolved gases to marine biota, assessing watermass movements, and minimizing underwater corrosion. Shipboard measurement of dissolved O_2, N_2, Ar, CO_2, CO, CH_4, NO_2, CCl_4, H_2, freon, and light hydrocarbons in seawater and the atmosphere. Significance and relationship of dissolved gases to marine biota are being studied in cooperation with NRL biologists. Gas exchange is being investigated between seawater, gas bubbles rising in the water column, and the atmosphere.

B.3.2 Biological Indicators

The following discussion of biological indicators has been separated from the discussion of other emerging methods of pollution assessment (Section 5.2.1) due to the current interest that biological indicators are receiving. In addition, the area of biological indicators is largely of a research status at present; development of monitoring applications is in its inception.

Although the majority of environmental monitoring programs address the levels of selected chemical contaminants in the environment as well as certain influential factors (such as currents, meteorological factors, etc.), the measurement of effects of pollutants and environmental degradation on marine organisms are less well developed but are receiving increased attention. The concentration of contaminants and their bioaccumulation in marine organisms have been investigated due to their implications for food chain availability to humans. However, the knowledge of the basic physiological and biochemical characteristics of marine organisms and the toxic effects that pollutants have on these organisms is quite limited. Currently, numerous researchers are investigating these factors with an interest in developing monitoring tools relying on biological indicators of ecosystem stress due to pollution. In particular it is felt that such indicators may be sensitive to subtle, chronic, low levels of pollution which may have long-term effects that will be significant but which might otherwise receive little attention since they are not signalled by ecosystem incidents. It is anticipated by most researchers that cause-and-effect relationships will be difficult to establish with these biological indicators (e.g., Teal et al., 1979, in reference 46). It has been noted elsewhere in this report that NOAA's Ocean Pulse Program will implement such biological indicators and the role of the ICES group in developing these tools has been discussed.

A broad range of pollutants representative of the various classes can be concentrated in marine organisms, where they might be present in tissue at various concentration levels and may reside for various lengths of time. Certain pollutants may be metabolized and detoxified by particular organisms or the organisms may excrete the pollutant and gradually cleanse themselves. Nevertheless, over the period during which the pollutant persists in the organisms, normal functioning of organic systems and metabolic processes may be disrupted. In individuals, mutagenic, teratogenic, and carcinogenic effects may result. The majority of toxicological information available for marine organisms is of limited value for quantitative evaluation due to natural variation within species populations, differences in experimental conditions and design, and differences in toxicants, species and physiological factors. In order to demonstrate cause-and-effect relationships between pollutants and biological responses, pollutant effects must be be distinguished from natural variability in living systems.

Pollutants may induce behavioral responses affecting the chemosensory and nervous system functioning of organisms. Consequently, alteration of feeding patterns, survival mechanisms or reproductive patterns may occur. Reproductive success and continued productivity are essential to both survival and utility of the species.

Continued research is necessary to the understanding of pollutant effects that will provide the basis for development of biological indicators for use in monitoring leading to accurate assessment and prediction. Determination of response patterns to pollutants with various systems and species potentially can permit estimation of the hazards associated with pollutants, the definition of areas affected, and may provide a basis for deducing cause-and-effect mechanisms of pollutants. Investigation of the effects of pollutants which leads to development of useful diagnostic biological indicators might be at the organ, organism, or system level in a given instance.

Bioaccumulation of contaminants by marine organisms which is often selective and sometimes spectacular (concentration factors of several hundred thousand times ambient concentrations have been reported for cadmium in marine molluscs) potentially provides a basis for successful monitoring of levels of these contaminants and changes in their availability in the environment. The U.S. Environmental Protection Agency has conducted its Mussel Watch Program based on this approach since 1976.(47) The program monitors trace metals, radionuclides, halogenated hydrocarbons, and petroleum hydrocarbons in mussels (Mytilus) and oysters (Ostrea and Crassostrea) at 100 strategically selected stations representing the three major U.S. shorelines serving as a network for annual monitoring of the pollutants. In order to assess seasonal changes in pollutants in these molluscs, samples have been collected and analyzed monthly from a station at Bogeda Head, California, and a station at Narragansett Bay, Rhode Island. Histopathological examination of the analyzed molluscs has been conducted to provide data on organ level condition of the organisms. In addition, relative concentration levels of pollutants in various organs in the molluscs have been investigated. Cause-and effect between pollutant stress and pathological conditions remains to be demonstrated although initial findings of the program indicate that methods of ascertaining sublethal biological effects of pollutants on mussel populations may result.

A study by Majori et al.(48) has special significance for the Mussel Watch approach. In their study, mussels (Mytilus galloprovincialis) were subjected to aqueous levels of 5, 50 and 500 ppb of Hg or Pb. It was found that they accumulated the metals until attaining an equilibrium concentration proportional to the pollution level. It was determined that, in the Gulf of Trieste, concentrations of Pb, Zn, and Hg in specimens were readily correlated with general environmental conditions and with the degree of metal pollution in the sediments in particular. It was observed that mussels which were transplanted from polluted to relatively "clean" areas gradually relinquished their metal burden although more slowly than the rate of metal accumulation observed when initially uncontaminated mussels were transplanted to polluted areas.

In other related work Phelps and Myers(49) investigated bioaccumulation as a function of organism (species), location and ecological niche in Narragansett Bay. Representative fauna were grouped in terms of feeding stratum in the environment such that organisms feeding below the sediment-water interface, those feeding at the sediment-water interface, and those feeding in the water column were distinguished. It was determined that for chromium, water column feeders were the best indicators in that they had higher concentrations than were found in the other groups. Interface feeders exhibited slightly higher concentration factors for silver and zinc than in the other two groups. Subsurface feeders had slightly lower concentrations than did the other two groups. Subsequent to identification of water column feeders as the best indicator group, the metals determined for that group were expanded to include Cr, Zn, Cd, Ag, Cu, Pb, Ni, Co, Mn, Ti and V. Measurement of these metals in tissues of water column feeders obtained along a sampling transect revealed that concentrations varied abruptly rather than gradationally toward concentration highs. No significant seasonal changes in tissue concentration were found with time series data. Depuration studies were also conducted with the organisms. Three types of results were obtained. Organisms which exhibited high tissue levels of Cd, Cu, Ni, Pb and Ti continued to be concentrated in these metals after 30 days depuration. For Mn, Zn, V and Co there were no significant differences between contaminated and uncontaminated areas prior to or following depuration. For Ag apparent differences observed upon collection were eliminated following depuration.

A study of bioaccumulation in tunicate (subphylum of marine chordates) species by Popoudopoulou and Kanais(50) employed neutron activation analysis to determine concentrations of Co, Zn, Cr, Cs, Ag, Fe, Rb, Se, Sc and Sb. One species was found to be a specific bioaccumulator of Fe; another species was determined to be a good indicator for Se, Cr, Zn and Co.

Numerous studies have been conducted on toxicity of pollutants to marine organisms although the extent of such information will probably remain inadequate for some time given the number of marine organisms which might serve as indicators and the number of contaminants which might be investigated. Furthermore, the standardization of methods and criteria in such toxicity tests is an obvious problem. Peltier(51) attempted to provide guidelines for test species selection and handling as well as data interpretation in conducting short- and long-term LC_{50} toxicity determinations with macroinvertebrates and fish. Persoone and Dive(52) have proposed methods to study the toxicity of chemicals or environmental pollution on ciliates as representative test organisms of the microfaunal assemblage of aquatic ecosystems based on morphological, ultrastructural, and metabolic criteria. Techniques proposed are largely species dependent as are their application and limitations. Considering the likelihood of future standardization of protozoan toxicity tests, a selection of tools was made considering the applicability of the tests for routine analysis.

Recent studies have examined behavioral phenomena of organisms as indicators of ecosystem pollutant stress. Cripe(53) reports findings with a AGARS (Aquatic Gradient Avoidance Response System) device. Whereas most apparatus designed to detect avoidance of pollutants by aquatic organisms involves visual observations of test organisms in the presence of steep pollutant gradients, the GAARS device overcomes these limitations. The system utilizes infrared light sources, sensors, and microprocessors to monitor the preference exhibited by organisms between four zones where one is maintained in an uncontaminated condition and three others with progressively higher levels of a toxic contaminant. Data were accumulated hourly as to the relative time over which test organisms remained in each zone; behavior prior to and during test exposures were compared. Avoidence effects of chlorine-produced oxidants with pinfish were investigated. A recent study by Morgan(54) reports the use of lightbeam interruption methods to monitor fish movement patterns under various conditions of acute and sublethal concentrations of toxicants. Success was reported with the technique for a wide variety of contaminants; limits of response to various contaminants were determined. In an earlier study, Morgan(55) reported the use of fish opercular rhythm response to monitor pollutants. Respiratory response of fish to lethal and sublethal toxicant concentrations was reported to be a reliable parameter for use of automonitoring systems. In a study by Wordingham,(56) aspects of fish behavior were examined as indicators of water quality changes in rivers and estuaries. Parameters measured included signals produced by muscles of fish during movement of the heart and opercula as well as general body movement.

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APPENDIX C

STANDARD ANALYTICAL
LABORATORY METHODS

C.1 INTRODUCTION

The following Appendix is a compilation of standard analytical laboratory methods for the determination of the oceanographic and pollutant parameters which are currently of interest to NOAA programs. The list of parameters for which methods are provided corresponds to those in Table 2-2. Numbers assigned to each parameter in column 5 of Table 2 correspond to the parameter method(s) given in the following. This information has not been obtained from various sources so that information is not consistently available in the same form for each parameter and method. For example, the precision of some methods has been reported as percentage values. In other cases, the source document provided results in terms of precision. For most methods, a brief description of the procedure, data on analytical range, precision, and interferences are provided. Although this is a compilation for laboratory methods, many are adaptable to ship-board use and *in situ* measurement and this is noted in some instances. In addition, *in situ* and field methods are described separately in Section 4.2. A description of analytical methods, a discussion of some of the principal standard laboratory instrumentation and their capabilities are provided in Section 4.1.

C.2 STANDARD METHODS

1.) Dissolved oxygen

a.) Modified Winkler Method

The method described in reference 1 for dissolved oxygen determination for seawater is a modification of the classical Winkler procedure. The procedure involves the addition of manganese sulfate solution and an alkaline iodide solution to the sample. Dissolved oxygen in the sample oxidizes and equivalent amount of manganese to yield hydroxides of manganese with higher valence states than the bulk of the manganese hydroxides precipitated from the solution. Subsequent acidification of the sample, in the presence of iodide, causes the oxidized manganese to revert to its divalent state and is occasioned by liberation of iodine equivalent to the original dissolved oxygen content of the water. This iodine can be titrated with standardized thiosulfate solution. Electrochemical end point detectors may be used although the classical starch end point method gives a comparable precision. The method enables dissolved oxygen measurements in the range from aproximately 0.1 to 120 mg/liter. The precision obtainable with the method is approximately ±0.5% for samples containing 10 mg/liter dissolved oxygen. This would correspond to the highest precision obtainable in a shore-based laboratory. However, at sea under routine conditions, the uncertainty could be doubled.

b.) Conductivity methods

Reaction of neutral aqueous species with dissolved oxygen to produce ionic species is the basis of several conductivity methods for DO determination as discussed in reference 2. For example, one method depends on the oxidation of nitric oxide gas by the dissolved oxygen in the same to produce nitrite ion, thereby increasing the conductivity of the sample, which is measured prior to and after its reaction with nitric oxide gas in a saturator.

Other conductivity methods rely on the reaction of dissolved oxygen with metallic lead and metallic thallium; a commercial apparatus for dissolved oxygen determination is based on the latter reaction. Conductometric methods provide detection limits of a few parts per billion.

2.) Nitrate

The method of analysis for nitrate in seawater is described in reference 1 and is based on a method of Morris and Riley (1963). The nitrate in seawater is reduced almost quantitatively to nitrite upon passing the sample through a column containing cadmium filings coated loosely with metallic copper. The resulting nitrite is determined by diazotizing with sulpharilamide and coupling with N-(1-naphthyl)-ethylenediamine to produce colored azo dye, the optical density of which is measured spectrophotometrically. A correction may be made for any nitrite initially present in the sample. The method has an analytical range of 0.005 through 2.5 mg/liter NO_3 and a precision of approximately ±2.5%.

3.) Nitrite

The method of analysis of nitrite in seawater described in reference 1 involves the diazotization of sulfarilamide by NO_2 in acidic aqueous solutions along with N-(1-naphthyl)-ethylenediamine to produce a reddish-purple colored azo dye measured at 540 nm. Strong oxidants and reductants affect NO_2 concentration. High alkalinity suppresses color formation. This method enables determination of nitrite ion in the range of 0.5 to 100 mg/liter with a precision of approximately ±3.0%.

4.) Phosphate

Most methods for determination of phosphate in seawater are based on the formation of a phospho-molybdate complex and its reduction to strongly blue-colored compounds. Ammonium molybdate and potassium antimonyltartrate react in acid medium with orthophosphate ion to form an antimony-phospho-molybdate complex. Reduction of the complex by ascorbic acid is followed by absorbance measurement at 880 nm. This method enables determination of phosphate in the range of 0.003 to 0.5 mg/liter; its precision is approximately ±1%. The procedure is both rapid and convenient and therefore advantageous for analysis at sea.

5.) Silica

There are a number of methods for the determination of silica in aqueous solution including seawater. Many of these are based on the production of yellow silicomolybdate complex. Direct measurement of light absorption may be done spectrophotometrically for this complex. However, reduction of the complex to a blue compound results in a more sensitive analytical procedure and results in optical density values that are more stable with time. In the method described in reference 1, the seawater sample is treated with molybdate under conditions resulting in the formation of silicomolybdate, phosphomolybdate, and arsenomolybdate complexes. A reducing solution with metol and oxalic acid is added. This reduces the silicomolybdate complex to a blue compound and decomposes any phosphomolybdate and arsenomolybdate eliminating such interferences. Extinction should be measured at 810 nm. The method has an analytical range from 0.01 to 8 mg/liter and a precision of approximately ±2.5%.

6.) Ammonia nitrogen[4]

Ammonia nitrogen in seawater may be determined by the distillation procedure. The sample is buffered at pH = 9.5 to inhibit hydrolysis or organic nitrogen compounds, distilled into a boric acid solution and the ammonia nitrogen determined colorimetrically by Nesslerization or acidimetrically with standard sulfuric acid using methyl red indicator. Glycine, hydrazine and some amines may react with Nessler's reagent and thereby interfere in the determination. Hydrazines and amines also affect results of the titrimetric procedure. The method has an analytical range of 1 to 25 mg/liter ammonia nitrogen and a precision of ±2.0%.

7.) Turbidity[4]

a.) Jackson Candle turbidity

This method is adequate for the measurement of light-scattering by turbid water, but it is insufficiently sensitive for measurement of turbidity of filtered water (or clarified waste effluents). The Jackson Candle method provides empirical measurements of turbidity based on column liquid depth of sample (in a special graduated vessel) that is sufficient is extinguish the image of a standard candle or other light source observed through the sample column. Turbidity measurement is made by pouring sample suspension into the sample tube to the extinction point of the image. The depth of suspension required to reach this point is converted to a corresponding Jackson turbidity number (between 25 and 1000) obtained from a value table.

b.) Nephelometric turbidity

Nephelometric turbidity determination is accomplished by measuring scattered light intensity at right angles to an incident light beam. Nephelometers cannot be calibrated accurately in terms of absolute turbidity except in suspension with particles of rather uniform size less than approximately one-fifth the wavelength of the incident light. After calibration of the instrument with turbidity standards, nephelometric turbidity of samples may be calculated from the known relationship of nephelos units to instrument units.

c.) Absolute turbidity

Measurement of absolute turbidity employs an integrating sphere apparatus to measure both scattered and transmitted light. The method measures all the scattered light (not simply normal to the incident beam) and alleviates the particle size limitation. However, if particle size of suspensions is great enough that back-scattering is negligible, instrumental complexity can be reduced. Absolure turbidity of samples is computed from the ratio of total scattered light intensity of the integrated transmitted and scattered light intensity.

8.) <u>Membrane Filter Procedure for Total Coliform Bacteria</u>

Methods for determination of coliform are presented in <u>Standard Methods</u> (Standard Methods for the Examination of Water and Wastewater, 1971, American Public Health Association, Washington, D.C., 13th Edition, pp. 678-683). Experience has indicated that the membrane filter technique is applicable to the examination of fresh and saline waters. Turbidity due to algae or other interfering material may prevent obtaining significant results and low coliform counts may be caused by the presence of high numbers of noncoliform or of other substances. Methods are available which employ agar-based medium or M-Endo medium without agar.

Generally, an enrichment procedure gives best results. However, such an enrichment step may be eliminated in routine examination where it has been demonstrated that adequate results are obtained by a single step direct technique.

The sample (20 to 50 ml) is filtered under partial vacuum onto an initially sterile filter. Filtration units should be sterile at the beginning of each filtration series to avoid accidental contamination. Rapid decontamination of the equipment between successive filtrations may be accomplished by use of an ultraviolet (UV) sterilizer, steam or boiling water.

If agar-based medium is employed, the prepared filter is placed directly on the agar. The filter is incubated for 22-24 hrs at 35 ±0.5°C. If the liquid medium is used, a pad is placed in the culture dish and saturated with 1.8 to 2.0 ml of M-Endo medium. The prepared filter is placed directly on the pad and incubated for 22-24 hrs at 35 ±0.5°C.

Typical coliform colonies have a pink to dark red color with a metallic surface sheen. The area of sheen may be localized or cover the colony surface. Counts are best performed by aid of a low power, binocular, wide-field dissecting microscope.

The calculated coliform density is reported in terms of total coliforms per 100 ml. Computation is based on a membrane filter count within the 20 to 80 coliform range and is in accordance with the following equation:

$$\text{(Total) Coliform Colonies/100 ml} = \frac{\text{Coliform Colonies Counted} \times 100}{\text{ml of Sample Filtered}}$$

If membrane filter counts are less than 20, all such counts should be totaled and the value based on the overall volume of sample used (i.e., combined volumes). Sample volumes to be filtered can be adjusted in order to yield coliform densities that can be worked with conveniently and accurately.

9.) Salinity

The dissolved salts content of seawater is usually expressed as salinity (S, parts per thousand) which would be obtained through calculation based on dry weight of solids in 1 liter of seawater after oxidation of the organic matter, replacement of bromides and iodides by equivalent amounts of chloride, and conversion of carbonates to oxides. A standard method for salinity is described in reference 1.

The determination of salinity is accomplished by measuring chlorinity (Cl, parts per thousand) and calculating salinity from the Knudson equation:

$$S = 0.03 + 1.805 \text{ Cl}$$

The chlorinity of seawater is defined as 0.3285234 times the weight of silver precipitated from seawater upon titration with silver nitrate. The titration uses a chromatic end point (the Mohr titration). Standardization of the silver nitrate solution is achieved by titrating a standard seawater sample of known chlorinity. Corrections are made for temperature and density. At a typical salinity of 33 parts per thousand, a precision of 0.07 percent can be obtained.

Salinity measurements may also be obtained through electrical conductivity, density, or optical means (refractivity). However, the method of silver nitrate titration remains an internationally acceptable method offering convenience and high precision.

10.) Plankton

The term "plankton" applies to microscopic and near-microscopic, free-floating organisms which include, among the phytoplankton, Chrysophyta (diatoms and related forms), Chlorophyta (green algae), Cyanophyta (blue-green algae), and Eumycophyte (fungi). Among the zooplankton are Protozoa, Rotifera, Crustacea, Porifera, and Bryozoa. Immature insects and small worms present are also considered as plankton. "Total plankton" may be obtained by sedimentation of plankton in water samples. Sampling for the estimation of total plankton involves collection of water samples with stopped glass bottles or special samplers capable of collecting water at any desired depth. Special samplers include the Kemmerer water bottle, Hale's sampler, Irwin's sampler and pump samplers. Alternatively, a fraction of the plankton population may be obtained by straining the water through a fine-mesh cloth. The organisms collected in this manner are known as net plankton (macroplankton). Sample examination conducted with live organisms is adviseable for highest accuracy. However, substantial care is required to prevent deleterious sunlight exposure of the sample, oxygen exhaustion or temperature increase since planktonic organisms are especially sensitive to such environmental changes. If the sample is not to be examined fresh, it should be preserved promptly after collection by the addition of formalin (approximately 5 ml of formalin to each 100 ml of sample).

The plankton fraction is examined microscopically and results reported in various ways as desired. For example, the numbers of organisms of various species may be determined directly or a conversion of such numbers to volumes of plankton species may be reported. Such volumetric conversion involves applying a factor based on average or representative volume determined for each species.

11.) Chlorophyll

a.) Spectrophotometric determination

The determination of chlorophylls and total carotenoids may be accomplished spectrophotometrically. This determination of characteristic plant pigments (chlorophylls, carotenes, and xanthophylls) is related to the quantity of phytoplankton in seawater, but the amount of organic substance associated with a given quantity of plant pigment is quite variable and will depend on the class of phytoplankton and state of nutrition. Consequently, the factor for converting chlorophyll a to total plant carbon may range between 25 and 100.

The method described in reference 1 determines the three chlorophylls common in phytoplankton algae (chlorophyll a, b, and c). The procedure involves filtering 0.5 to 5 liters of seawater through 0.3 mm nylon mesh to remove large zooplankton. A small amount (0.2 to 0.3 ml) of magnesium carbonate suspension is added. At this point the sample can be stored under dark, cool conditions for no more than 8 hours. Preferably, samples should be filtered (through a membrane filter) at the time of collection. Such filtered samples can be stored for prolonged periods (up to several weeks) although this makes subsequent extraction of chlorophyll more difficult; filters should be extracted promptly if possible. The pigment is extracted by dissolving the filter in acetone and refrigerating the sample in the dark for 20 hours. The sample is then centrifuged and the final supernatant liquid transferred to spectrophotometer cells for measurement of extinction values. The extinction values are measured against 90% acetone at 750, 665, 645, 630 and 480 nm. With these extinction values, simple linear equations permit computation of the quantity of each of the pigments (chlorophyll *a*, *b*, and *c*) in the sample. The concentration of the pigments in seawater is then computed by dividing the quantity of pigment in milligrams by the original volume of the seawater sample. The lower limit of detection by this method is approximately 0.02 mg/liter for chlorophyll *a* and 0.04 mg/liter for chlorophyll *b*. The precision for chlorophyll *a* is approximately ±5% although poorer for chlorophyll *b* and *c*.

Chlorophyll degradation products may complicate the analysis and its interpretation. Chlorophyllide will go undetected by the method and will be reported as an equivalent weight of chlorophyll. Any phaeophytin or phaeophorbide will lead to a decrease in the 665 nm extinction; these pigments will go undetected and be reported as if about half the amount of chlorophyll were present. An estimate of the amounts of phaeopigments present in samples may be obtained by measuring extinctions (or fluorescence) before and after acidification of extracts.

b.) Fluorometric determination

Reference 1 describes a method of chlorophyll determination by fluorometry. Extracts are obtained in the same manner as described in the foregoing spectrophotometric method. The fluorometer utilizes filters for both the illuminating (excitation) light and the emitted light. The method determines chlorophyll a only. Again, the detection limit depends on the volume of seawater filtered. However, for a 2-liter sample, 0.01 mg chlorophyll a per cubic meter is detectable. This method is not as accurate as the spectrophotometric approach but is faster and does not require as large a sample for a given sensitivity. The precision is approximately ±8% at levels of chlorophyll a exceeding 0.5 mg/m^3.

12.) Total Organic Carbon (TOC)[4]

a.) Oxidation-infrared detection

This method enables the determination of total and organic carbon in water, wastewater, and brines for concentrations of 2 to 200 mg/liter. After homogenization or dilution of the sample, as necessary, a micro portion of the sample is injected into a heated, catalyzed reaction zone of a furnace unit in which the carbonaceous matter is converted to carbon dioxide. A flowing gas stream carries the gaseous reaction products through a detector (e.g., nondispersivetype infrared stream analyzer set for carbon dioxide). The detector output signal or peak height is proportional to the carbon content of the sample and is quantified by referring to a calibration curve prepared from known carbon content standards.

Since carbon dioxide is liberated from carbonates in addition to organic matter under the total carbon test conditions, it may be necessary, in some instances, to modify the procedure to distinguish between organic and carbonate-derived carbon dioxide. For example, if the sample is acidified to a pH of 2 and sparged with a carbon dioxide-free gas, carbonates and biocarbonates will be removed. The remaining solution can then be analyzed for total organic carbon which will correspond to the amount present initially as organic carbon.

b.) Reduction-flame ionization detection

This method enables determination of total and organic carbon in the range from 1 to 2000 mg/liter in water, wastewater, and brines. After homogenization or dilution, as necessary, an acidified sample is injected into a sample boat and advanced to the 115°C zone of a pyrolysis furnace where CO_2, H_2O, and volatile (at 115°C) organic carbon are swept by helium into the bypass column. Here, volatile organic carbon is trapped on an absorbent at 60°C while the CO_2 is swept through the switching valve and vented to atmosphere.

After vaporization of the sample, the valve is automatically switched to the pyrolyze position and the bypass column is backflushed at 130°C. The volatile organic carbon is swept by helium flow through the pyrolysis zone and into the hydrogen-enriched, nickel catalyst reduction zone at 350°C where it is converted to methane. The methane is then swept into the flame ionization detector which responds linearly to methane. Subsequently, the sample boat is advanced to the pyrolysis zone where residual organic carbon left in the boat reacts with the oxidizer at 850°C to produce CO_2 which is converted to methane that is swept into the flame ionization detector. The combined readings (for the volatile organic carbon and residual organic carbon) are compared to a calibration curve obtained with standard potassium hydrogen phthalate solutions. The majority of instruments can be adjusted, through calibration, against the standards, to give direct readout in mg/liter of carbon.

13.) Lead[4]

a.) Direct atomic absorption

Dissolved and total recoverable lead in most waters and wastewaters is determinable in the range from 1.0 to 10 mg/liter by direct atomic absorption. The upper limits of detectability can be increased by dilution of the sample. Dissolved lead is determined by aspirating the filtered sample directly with no pretreatment. Total recoverable lead is determined by aspirating the sample following hydrochloric-nitric acid digestion and filtration. Standardization and calibration may be accomplished by comparison of absorbance values with an analytical curve prepared from a set of standard solutions. Many instruments may be programmed to give direct readout in concentration units. Typically, other metals do not interfere in lead determination by increasing or decreasing the amount of radiation absorbed. The most frequent interference results from a chemical reaction in the flame that prevents conversion of lead to atomic state. High concentrations of calcium can cause lead determinations which exceed actual concentrations. There are various measures which can be employed to overcome this interference. The chelation-extraction procedure (described subsequently) is one such means of decreasing interferences. Determination of lead by direct atomic absorption is reported to have a precision of ±10% at a concentration of 1 ppm in the sample.*

b.) Atomic absorption with chelation-extraction

Dissolved and total recoverable lead in the concentration range of 100 to 1000 parts per billion may be determined by atomic absorption, chelation-extraction method. Lead in dissolved and total recoverable forms is chelated with pyrrolidine dithiocarbanic acid and extracted with chloroform. The extract is evaporated to dryness, treated with hot HCl and diluted to a predetermined volume with water. The resulting solution is then aspirated into the air-acetylene flame of the spectrophotometer for analysis. As noted above, this chelation-extraction procedure reduces the potential for

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*For methods of trace element analysis determinations obtained from the ASTM manual, precisions are stated based on inter-laboratory comparisons and are thus much higher than single operator precision.

analytical interferences. A precision of ±12% can be obtained by this method at a concentration of 100 ppb in the sample.

14.) Mercury

The ASTM standard test method[4] for total mercury in water is by cold vapor atomic absorption. Mercury present as organic or inorganic forms may be determined by this method after conversion to mercuric ions by the use of oxidants (e.g., potassium permanganate) with digestion at 95°C. The mercuric ions must then be reduced to metallic mercury (with stannous sulfate solution). Mercury vapor arising from the sample is pumped to an absorption cell for the cold vapor atomic absorption measurement. The method covers determination of total mercury in water in the range from 0.2 to 10 ppb Hg/liter and is applicable to saline and fresh waters.

15.) Chromium

a.) Direct atomic absorption

Total chromium in water is determinable in the range from 0.1 to 10 mg/liter by atomic absorption spectrophotometry. The range may be extended to concentrations greater than 10 mg/liter by dilution of the sample. The lower limit of detectability is largely dependent on equipment employed in atomic absorption spectrophotometry. The lowest concentration of the metal that can be determined is affected by the type of burner, length of flame path, fuel, oxidant, energy source, and the degree of electrical expansion of the output signal. The minimum measurable concentration is usually considered to be equal to twice the maximum variation of the background. Dissolved chromium is determined by directly aspirating a portion of the filtered sample with no pretreatment.

Interferences potentially arising from dissolved iron, nickel, and cobalt are eliminated in samples which have been adjusted to 1% ammonium chloride in concentration. Sodium, sulfate, and chloride (at 9000 mg/liter each) do not interfere.

b.) Spectrophotometric methods

ASTM standard tests[4] for total chromium in water include various spectrophotometric methods which depend on color reaction between sym-diphenyl carbazide in acid solution. These are:

	Applicable Concentration Ranges (mg/liter)	Precision
Permanganate oxidation	0.5 to 5	2-15%
Hypobromite oxidation	0.5 to 5	2-15%
Alkaline-Persulfate oxidation	0.5 to 5	3%

These methods rely on oxidation of chromium to the hexavalent form in order to achieve quantitative colorimetric determination. By first removing hexavalent chromium (chromate) from the sample with anion exchange resin, the remaining trivalent chromium can be determined by the alkaline-persulfate method thereby enabling determination of chromium in both valence states. Interferences with these colorimetric methods can result if oxidation of organic matter is incomplete, or if iron, phosphate, or chloride is excessive.

16.) Cadmium[4]

a.) Direct atomic absorption

Dissolved and total recoverable cadmium are determinable in waters and wastewaters in the range from 0.05 to 2 ppm by direct atomic absorption spectrophotometry. Cadmium concentrations greater than 2.0 ppm can be determined after sample dilution. Dissolved cadmium is determined by aspirating the filtered sample with no pretreatment. Total recoverable cadmium is determined by aspirating the sample subsequent to hydrochloric-nitric acid digestion and filtration. Calcium concentrations above 1000 ppm suppress cadmium absorption. Interference does not occur with sodium, potassium, sulfate and chloride concentrations as high as 9000 mg/liter or with iron or magnesium as high as 4000 mg/liter. Nickel, lead, copper, zinc, cobalt, or chromium as high as 10 mg/liter each do not interfere. The precision of the direct atomic absorption determination of cadmium is reported as ±10% at a concentration of 1 ppm in the sample. (See footnote on precision for lead.)

b.) Atomic absorption with chelation-extraction

This method enables the determination of dissolved and total recoverable cadmium in waters and most brines where cadmium is present in concentrations from 5 to 200 ppb concentrations exceeding 200 ppb following sample dilution. Either dissolved or total recoverable cadmium is chelated by pyrrolidine dithiocarbanic acid and extracted with chloroform. The extract is evaporated to dryness, treated with hot nitric acid (to destroy organic matter), dissolved in hydrochloric acid, and diluted to a specified volume with water. The resulting solution is aspirated into the air-acetylene flame of a spectrophotometer. The digestion procedure for total recoverable cadmium is accomplished by hydrochloric-nitric acid treatment of the sample followed by filtration. The remarks on interferences affecting this method are the same as those described for method (a) for cadmium. The precision of the atomic absorption, chelation-extraction method for cadmium is ±12% at a concentration of 100 ppb in the sample. (See footnote for precision on lead.)

17.) Arsenic (standard ASTM test methods for arsenic in water and wastewater)

a.) Atomic absorption-hydride generation

Dissolved and total recoverable arsenic in the range from 1 to 20 ppb are determinable by this method. Organic arsenic-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The arsenic (V) so produced, together with the inorganic arsenic initially present, is then reduced to arsenic (III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The arsine is removed from solution by aeration and swept (by a flow of nitrogen) into a hydrogen flame for determination by atomic absorption spectrophotometry.

Several metals, notably cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum, may interfere with the evolution of arsine. The extent of any such interference can be determined by spiking.

b.) Silver diethyldithiocarbamate colorimetric

Dissolved and total recoverable arsenic in the range from 5 to 250 ppb are determinable by this method. The procedure is the same as that of method (a) up to the point of generation of arsine by zinc in the acidified sample. The arsine is passed into an absorption tube containing a solution of silver diethyldithiocarbamate in pyridine with which it reacts to form a red-colored sol. The absorbance of the solution is measured spectrometrically and the arsenic determined by reference to an analytical curve prepared from standards. Interferences with the generation of arsine potentially resulting from the presence of various metals are the same as with method (a). Table C-1 shows the results of precision studies with arsenic test methods.

18.) Selenium

The method for analysis for selenium in surface water and wastewater is as follows:[5]

Acid permanganate is used to oxidize selenium to selnate and subsequently reduced to selnite which is then reacted with diaminobenzidene to form piazselenol complex. The complex is extracted into toleune and absorbance measured spectrometrically at 420 nm. The

TABLE C-1

RESULTS OF PRECISION STUDIES WITH ARSENIC TEST METHODS

Method (a)			Method (b)		
Amount Added, ppb	Amount Found, ppb	± Bias	Amount Added, ppb	Amount Found ppb	± Bias
3.0	3.16	+0.16	25.0	23.66	-1.34
10.0	9.74	-0.26	100.0	95.28	-4.72
18.0	17.67	-0.33	200.0	194.99	-5.01
5.0	1.99	-3.01	50.0	32.14	-17.86
3.0	2.70	-0.30	25.0	24.76	-0.24
10.0	8.76	-1.24	100.0	97.00	-3.00
18.0	18.07	+0.07	200.0	189.01	-10.99
5.0	2.13	-2.87	50.0	22.83	-27.17

analytical range of the method is 0.003 to 0.05 ppm selenium. Temperature, pH and time control are necessary for reliable results. Ferric iron (Fe^{3+}) interference can be eliminated by EDTA. Interference due to bromide (Br^-) and iodide (I^-) may be eliminated by oxidative distillation with $KBr-N_2SO_4$ and H_2O_2.

19.) Silver

The method of analysis for silver in surface water and wastewater is as follows:[5]

Direct atomic absorption spectrophotometry at 328.1 nm enables determination of silver with an analytical range of 0.1 to 20 ppm. A detection limit of 0.01 ppm can be obtained with this method. Higher concentrations of silver can be determined at 338.2 nm.

20.) Copper[4]

a.) Direct atomic absorption

Dissolved and total recoverable copper in most waters and wastewaters may be determined by atomic absorption spectrophotometry. The method enables measurement of copper in the range from 0.02 to 5 ppm and may be extended to higher copper concentrations by dilution of the sample. Dissolved copper in filtered samples is determined by aspirating the sample directly with no pretreatment. The determination of total recoverable copper is accomplished after digestion with hydrochloric-nitric acid and filtration. Interference does not occur with sodium, potassium, sulfate and chloride at 8000 mg/liter each; calcium and magnesium do not interfere at 5000 mg/liter each; iron does not interfere at 1000 mg/liter; cadmium, lead, nickel, zinc, cobalt, manganese, and chromium do not interfere at 10 mg/liter each. The precision of copper determination with this method is reported as ± 9% at a concentration of 5 ppm in the sample. (See footnote for precision on lead.)

b.) Neocuproine method

Colorimetric determination of copper in water and wastewater may be accomplished based on measurement of the intensity of the yellow cuporous complex of 2,9-dimethyl-1,10-phenanthroline (neocuproine). Complete color development takes place throughout the pH range from 2.3 to 9.0 although a pH buffer is used to maintain pH between 4.0 and 6.0. The procedure involves reducing the available copper with hydroxylamine hydrochloride and adjustment of the pH with a sodium citrate solution. Cuprous ion is then reacted with 2,9-dimethyl-1,10-phenanthroline and the yellow complex extracted with chloroform for subsequent measurement by usual photometric methods or visual comparison. This method enables measurement of copper in the concentration range of 0.05 to 5.0 ppm with a precision of approximately 1%.

21.) Thallium

A method for the determination of thallium by atomic absorption spectrophotometry is given in Methods for Chemical Analysis of Water and Wastes (U.S. Environmental Protection Agency, 1976). The determination of thallium by this method has an optimum concentration range of 1-20 mg/l using a wavelength of 276.8 nm. A sensitivity of 0.5 mg/l and detection limit of 0.1 mg/l are obtainable.

For determination of dissolved thallium, the sample is first filtered through a 0.45 membrane filter as soon as practical after collection. The filtrate is acidified with 1:1 redistilled HNO_3 to a pH of 2; normally 3 ml of (1:1) redistilled HNO_3 to a pH of 2 at the time of collection. A representative aliquot of well-mixed sample is transferred to a Griffin beaker and 3 ml of concentrated redistilled HNO_3 is added. The beaker is placed on a hot plate and evaporated to dryness although boiling should be avoided. Next, the beaker is cooled and another 3 ml of concentrated, redistilled HNO_3 is added. The beaker, covered with a watch glass, is returned to the hot plate. The alternate heating and addition of acid is continued until digestion is complete. Sufficient distilled 1:1 HCl is added followed by heating to dissolve any residue. The beaker walls and watch glass are washed down with distilled water and the sample filtered to remove insoluble matter such as silicates that could clog the atomizer. The sample is adjusted to a predetermined value based on expected metal concentration. Determination of thallium in the sample can now be done on the spectrophotometer. Calibration is accomplished by measurement of absorption with a set of thallium standard solutions.

Instrumental parameters for thallium analyses are:

1. Thallium hollow cathode lamp

2. Wavelength: 276.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: oxidizing

A precision study has been conducted by the Methods Development and Quality Assurance Research Laboratory of the National Environmental Research Center (Cincinnati, Ohio) for thallium using this method for a mixed industrial-domestic waste effluent at concentrations of 0.60, 3.0 and 15 mg Tl/l. Standard deviations were ±0.018, ±0.05 and ±0.2, respectively. Recoveries at these levels were 100% and 98%, respectively.

This method for thallium was found in:

U.S. Environmental Protection Agency (1976). Methods for Chemical Analysis of Water and Wastes, Environmental Monitoring and Support Laboratory, Environmental Research Center, Cincinnati, Ohio, p. 149.

22.) Plutonium

Methods for determination of plutonium include those which are macro-methods (applicable to samples containing >1 mg. plutonium) and micro-methods (applicable to samples containing <1 mg. plutonium). Macro methods used are oxidation-reduction titrations, direct spectrophotometry, X-ray absorptiometry, and X-ray emission spectrophotometry. Important micro methods in use are alpha counting, mass spectrometry by isotopic dilution, spectrophotometry of complex ions, polarography, and microcoulometric titration.

a.) Direct spectrophotometric methods

Plutonium can be determined by the direct absorptiometry of its ions in solutions or by the absorptiometry of certain highly colored complexes with organic reagents. Analytically useful absorption bands are present at various wavelengths, particularly at 602 nm for Pu(III), 470 nm for Pu(IV), 569 nm for Pu(V), and 833 nm for Pu(VI).

Direct spectrophotometry is employed for determining total concentrations at macro levels as well as determining the ratio of valence states in solutions. For the former application, plutonium is converted to a single valence state (i.e., either III or IV), and the absorbance of the particular species measured at the appropriate wavelength which is known from spectral data of plutonium ionic species in solution.

Direct spectrophotometric methods for plutonium can be employed for milligram quantities of plutonium with precisions in the range of ± 0.5 to ± 1%. The plutonium can be reduced to Pu(III) with hydroxylamine or other reagents, or oxidized to Pu(IV) with nitrate ion.

Improved spectrophotometric sensitivity for plutonium can be obtained by forming colored complexes with organic reagents. Even though many organic reagents form highly colored complexes with plutonium, few of these have been employed for analytical purposes (probably since alpha counting is more typically used). There are published spectrophotometric methods for Pu(IV) in the range of about 5 to 150 g of plutonium employing 2 (o-arsono-phenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonic acid (uranol,arsenazo) sodium alizarinsulfonate (alizarin red S), and (o-2-hydroxy-3,6-disulfo-1-naphthylazo)-bezenearsonic acid (thoron, thorin, or thoronol).

b.) Alpha counting methods

Low concentration levels of plutonium are most commonly measured by alpha counting. The method offers high specificity for plutonium when other alpha emitters are absent or the method is applied with suitable separation procedures. Since the specific activity of ^{239}Pu is 1.36 X 10^{11} alpha disintegrations per minute per gram and alpha counters with background rates of less than 1 count per minute are readily available, very minute amounts of plutonium can be determined. Therefore, alpha count methods are ideally suited to the determination of plutonium in waste process streams, biological materials, soil, water and in other media.

23.) Petroleum Hydrocarbons

Analytical methods for the determination of petroleum hydrocarbons (PHCs) have been summarized in reference 6 which points out that no single technique can be employed to determine all the various hydrocarbons in the marine environment. Analytical techniques cited in the following include those applicable to water, sediment, and tissue samples.

a.) Low-molecular-weight hydrocarbons

Low-molecular-weight (C_1-C_{10}) hydrocarbons are quite volatile, such that care must be taken during sample collection and preservation to avoid their loss to the atmosphere. Water can be sampled from virtually any depth with hydrographic equipment and sampling devices such as a Van Dorn water sampler. The following analytical methods are applicable to the low-molecular-weight hydrocarbons enabling resolution of individual hydrocarbons and hydrocarbon types. These each involve concentration or fractionation of hydrocarbons from the water sample prior to determination by gas chromatography.

Gas equilibration

The gas equilibration technique enables measurement of low-molecular-weight hydrocarbons in waters from all sources. A sensitivity of 1-3 ppt (parts per trillion) can be obtained for alkanes, alkenes, and cycloalkane hydrocarbons. Sensitivities of 8-10 ppt are obtained for aromatic hydrocarbons by this method. The method qualitatively separates hydrocarbons from water-soluble organics, therefore permitting their measurement in the presence of nonhydrocarbons without sample preparation. The amount of sample required is between 50 and 250 ml. The method is somewhat disadvantageous in requiring relatively lengthy analysis time.

Gas-stripping

Whereas gas equilibration enables background levels of methane in open seawaters to be measured, it has insufficient sensitivity for background levels of ethane, ethene, propane, and propene. Gas-stripping of 1 liter water samples can achieve these lower detection limits for the very light gases. However, the gas-stripping technique can confuse hydrocarbons with nonhydrocarbons in water. Additionally, analysis time is relatively long (10 to 30 min).

Vacuum degassing

Low-molecular-weight hydrocarbons (through C_4) have been continuously monitored at marine seep sites by detectors that separate gases from seawater by vacuum. Such systems are available commercially and offer sensitivity in the subpart per trillion range and can measure oceanic background levels of methane, ethane, ethene, propane, propene-iso, and normal butane. Such favorable results are due to the highly efficient partioning of low-molecular-weight hydrocarbons into the gas phase upon vacuum degassing. Analysis can be accomplished in from 3 to 30 min with samples in the range of 4 through 20 liters. Complete systems for vacuum degassing are expensive (complete ship-board system > $300K).

b.) Higher-molecular-weight hydrocarbons

Measurement of higher-molecular-weight (C_{11} and greater) hydrocarbons in seawater, as with the low-molecular-weight hydrocarbons, requires the versatility to measure the background levels of the open ocean through relatively high concentrations (e.g., in spill or natural seep areas). These procedures must also separate hydrocarbons from the solvent extractable nonhydrocarbon organics. Carbon tetrachloride (CCl_4) or other solvents are used to extract the hydrocarbons present prior to analysis. Several of these methods are described below.

Ultraviolet fluorescence spectrometry

In the ultraviolet fluorescence spectrometric method, the CCl_4 extract of the water sample is slowly evaporated to dryness and the residue subsequently dissolved in normal hexane. The excitation as well as emission spectra for this extract are scanned with a fluorescence spectrometer. Fluorescence intensities are compared with those of standard solutions representing a concentration range of a reference oil. Concentration of the unknown is determined by interpolation in waters with > 10 ppb of hydrocarbon with a precision of ± 10 percent for unsaturated and aromatic hydrocarbons. The technique does not provide information on saturated hydrocarbons. The UV fluorescence instrument (spectrometer) is in the $10K price range.

Liquid column chromatography

Uncertainties arising with non-hydrocarbons in the CCl_4 extract may be avoided if they are separated from the hydrocarbons. The total hydrocarbons are then analyzed by infrared, gas chromatography, mass spectrometry individually, or by combination of these techniques. Activated silica gel can be used in the separation procedure. After evaporation of the CCl_4 extract to 2 ml, 0.2 ml of n-pentane is added. The hydrocarbons are eluted with a CCl_4, n-pentane mixture yielding a saturate fraction; $CHCl_3$ elution yields an aromatic fraction. The hydrocarbon fractions can then be analyzed by the instrumental techniques noted above.

Infrared spectrometry

Infrared spectrometry is commonly employed for determining the low levels of hydrocarbons in seawater. Hydrocarbons may be concentrated from water samples by repeated extraction with high purity CCl_4. The extract may then be concentrated by evaporation and examined by IR to yield a measurement of total extractable organic compounds (the hydrocarbons as well as organic compounds such as alcohols and acids). Activated silica gel chromatography may then be used to isolate the hydrocarbons. With the proper accessories, a high-resolution IR spectrometer can determine hydrocarbons to approximately 1 ppb in a 6-liter water sample. Infrared spectrometry can determine methyl, methylene, carbonyl, aromatic, and total hydrocarbons. It can provide information on functional groups and can identify contaminants such as silicones and plasticizers.

24.) Polychlorinated Biphenyls

The ASTM tentative test method[4] for polychlorinated biphenyls (PCBs) in water is by gas chromatography following separation of PCBs and organochlorine pesticides from one another subsequent to a liquid-liquid coextraction. Detection and measurement is accomplished by using an electron capture, microcoulometric or electrolytic conductivity detector. Techniques for confirming qualitative identification are recommended. The method enables the determination of PCBs including: Arochlors 1221, 1232, 1242, 1248, 1254, 1260, and 1061. The method is designed so that PCBs and organochlorine pesticides may be determined on the same sample. Since PCBs may occur in the environment as both the unchanged commercial products and as metabolized and biodegraded products, quantitative determination of the class of compounds is often difficult to impossible. The detection limit of PCB mixtures (Arochlors) listed above is approximately 0.1 ppb. Results of a precision study indicated that a single operator precision of 10.2% is obtainable with Arochlor 1242 and 6.9% with Arochlor 1016 in river water. Unequivocal identification of PCBs present in sufficient concentration can be made by gas chromatographymass spectrometry (GC/MS).

25.) Pesticides

The ASTM tentative test method[4] for organochloride pesticides may be used to determine the following compounds: BHC, lindane, hepta-chlor, aldrin, heptachlor epoxide, dieldrin, endrin, Perthane, DDE, DDD, DDT, methoxychlor, endosulfan, -chlordane and Sulphanone. Under ideal circumstances, Strobane, toxaphene, Kelthane, chlordane, and others may be determined. Identification is by selective gas chromatographic separations through the use of two or more unlike columns. Detection and measurement is by electron capture, microcoulometric or electrolytic conductivity gas chromatography.

Pesticide analysis is frequently difficult due to the complexity of pesticide mixtures and the nature and the extent of interferences. Potential sources of interferences in pesticide analysis include plasticizers and hydraulic fluids such as chlorinated biphenyls. Depending to a degree on relative concentrations, chlorinated biphenyl isomers may interfere in the determination of DDE, DDD and DDT isomers. Data on precision of the method for organochlorine pesticides in water is presented in Table C-2.

TABLE C-2

PRECISION DATA FOR ASTM STANDARD TEST METHODS FOR PESTICIDES IN WATER[4]

Pesticide	Pretreatment	Mean Recovery, ng/liter	Precision ng/liter	
			°S	S_o
Aldrin	no cleanup	10.42	4.86	2.59
		79.00	32.06	20.19
	cleanup*	17.00	9.13	3.48*
		64.54	27.16	8.02*
Lindane	no cleanup	9.67	5.28	3.47
		72.91	26.23	11.94*
	cleanup*	14.04	8.73	5.20
		59.08	27.49	7.75*
Dieldrin	no cleanup	21.54	18.16	17.92
		105.83	30.41	21.84
	cleanup*	17.52	10.44	5.10*
		84.29	34.45	16.79*
DDT	no cleanup	40.30	15.96	13.42
		154.87	38.80	24.02
	cleanup*	35.54	22.62	22.50
		132.08	49.83	25.31

°S = overall precision, and
S_o = single-operator precision.
*Use of Florisol column cleanup prior to analysis

APPENDIX C REFERENCES

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LIST OF ABBREVIATIONS

AA - Atomic Absorption

AOML - Atlantic Oceanographic and Meteorological Lab.

B&W - Black and White

CIR - Color Infrared

CHRIS - Chemical Hazardous Response Information System

COE - Corps of Engineers

DO - Dissolved Oxygen

EDL - Engineering Development Laboratory

EPA - Environmental Protection Agency

ERTS - Earth Resources Technology Satellite

FDA - Food and Drug Administration

FWS - Fish and Wildlife Service

FY - Fiscal Year

GEK - Geomagnetic Electrokinetograph

GC - Gas Chromatography

GC/MS - Gas Chromatography/Mass Spectroscopy

HPLC - High Pressure Liquid Chromatography

ICAP - Inductively Coupled Argon Plasma Emission Spectrograph

ICES - International Council for the Exploration of the Seas

LAMPEX - Large Area Marine Productivity Experiments

MARMAP - Marine Resources Monitoring Assessment Prediction

M2S - Modular Multi-Spectral Scanning

MeI - Methyl Iodide

LIST OF ABBREVIATIONS (Continued)

MESA - Marine Ecosystems Analysis

MPRSA - Marine Protection, Research and Sanctuaries Act

NDBO - National Data Buoy Office

NEFC - Northeast Fisheries Center

NASA - National Aeronautics and Space Administration

NM - Nanometers

NMFS - National Marine Fisheries Service

NOS - National Ocean Survey

NOIC - National Oceanographic Instrument Center

ODP - Ocean Dumping Program

OCS - Outer Continental Shelf

OOE - Office of Ocean Engineering

PCB - Polychlorinated biphenyis

PCH - Polychlorinated hydrocarbons

PNAH - Polynuclear aromatic hydrocarbons

SOM - Subcommittee on Monitoring

SOTS - Sonar Oil Thickness Sensor

STAX - Sewage Tracking Experiment

TOC - Total Organic Carbon

VOA - Volatile Organics Analyzer

USCG - United States Coast Guard

XBT - Expendable Bathythermograph

XRF - X-ray Fluorescence Spectrometry

LIST OF ABBREVIATIONS (Concluded)

XWCC - Expanded Water Column Characterization Cruises

WSC - Water Sediment Chemistry

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