MULTITECHNOLOGY AND SUPPORTING RESEARCH PROGRAMS

- **Analysis of Natural Systems**
- **Quantitative Ecology of Impact Evaluation**
- **Effects of Water Quality Alterations on Fish Behavior**
- **Ecological Effects of Combined Aquatic Stressors**
- **Effects of Energy Systems Effluents on Coastal Ecosystems**
- **Bioavailability of Energy Effluent Materials in Coastal Ecosystems**
- **Marine Chemistry of Energy-Generated Pollutants**
- **In Situ Measurement of Pollutants**

This section includes research efforts that provide information applicable to several presently operating technologies as well as those being investigated for the future. In these technologies the nature of the environmental problem is equally applicable to any one technology; e.g., thermal and chemical pollution of water due to operation of steam electric plants, whether nuclear, fossil fuel, or gas fired; or, the statistical design needed for differentiating a general background of industrial pollution from the contributions, if any, arising from operation of an energy facility.

The two main groups of projects in this category include biomathematical effort represented by the first two projects indicated above and aquatic ecological studies represented by the remaining 5 projects.

Biomathematical Projects: These represent important effort in applying statistical theory to real-world problems such that appropriate error limits may be set when quantitative descriptions of ecological relationships are attempted. Specifically four areas of investigation are underway: 1) the application of sampling theory for the reliable measurement of environmental contamination, 2) methods for the statistical estimation of wildlife populations, 3) the evaluation of simulation models, and 4) statistical approaches for supplying an overview of large environmental data sets (e.g., pre- and post-operational monitoring data from steam-electric plants). In

addition to those projects covered in this section, an additional biomathematical project, described in Section 2, concerns the estimation of pollutant inventory at contaminated sites. The latter project concerns plutonium estimation at the NTS field site, but the approaches are applicable to other pollutants at heavily contaminated sites.

Aquatic Projects: These include both marine and freshwater studies and concern the bulk of Multitechnology Support effort. Generally, this research is directed at understanding the basic processes involved in the functioning of aquatic ecosystems. Several important developments in these programs will more clearly pinpoint the likelihood of actual biological impact from aquatic effluents. One development is the use of behavioral end-points for determining what organisms do in the natural environment. Isopleths of concentration for heat, gas saturation, or chemicals vary with depth and with location from an industrial plant. *In vivo* tagging procedures show that fish and other organisms may, in fact, remain outside the area of impact in certain situations. Another development is the move away from the single component bioassay, which is quite unrealistic, to multiple stressor ("synergistic effects") studies involving response surfaces. For example, we may now pinpoint a certain combination of heat, chlorine, and nickel concentrations, which when acting separately cause little or no mortality, but when acting together, produce 95-100% mortality. In the marine area, emphasis has been placed on establishing the extent of chemical speciation, target tissues, and the extent to which pollutants sorbed to sediments become biologically available. Pertinent related work will be found, also, in Section 2.

- **Analysis of Natural Systems**
- **Quantitative Ecology of Impact Evaluation**

Principal Investigators: L. L. Eberhardt and J. M. Thomas

Technician: M. I. Cochran

These projects have continued to be devoted to developing quantitative methods for broad use in applied and theoretical ecology. The wide array of technologies that must be dealt with in the present energy programs all have impacts on natural populations and man's environment. These impacts cannot effectively be evaluated without considerable improvements in quantitative methodology. We have thus continued an emphasis on sampling technology as it concerns both contaminants and animal populations. Census methods have also been emphasized, since they are essential to environmental studies and a considerable effort has been directed to the evaluation of mechanisms for animal population regulation, since this is a key item in "impacts." Direct evaluation of environmental effects of energy technology has been attacked this year by a detailed review of actual pre- and post-operational data on a number of sites. We thus hope to facilitate the development of efficient and effective field methodology.

Sampling for Contaminants

Our work on sampling for contaminants continues to emphasize issues in sampling methodology. As we have pointed out in several previous reports, it is possible to consider sampling methodology in four broad categories: 1) descriptive sampling, 2) analytical sampling, 3) sampling for spatial pattern, and 4) sampling for modeling. The available textbooks are mainly concerned with the first two categories. The first is the subject of the books with "sampling" in the title, while the second, although mentioned in the recent sampling books, falls between sampling methodology and the domain of "hypothesis-testing" statistical methods, e.g., the analysis of variance.

A technology of sampling for pattern has been evolving in the areas of mineral and hydrocarbon exploration, and has only very recently reached the stage where textbooks are available (Agterberg, 1974). Sampling for modeling has evolved largely in the areas of industrial research and experimentation, with statistical results largely available in journals like Technometrics. We have attempted to discuss some of the problems in applying sampling for pattern to radionuclides and other contaminants in two recent papers, and have given an illustration of the utility of sampling for modeling in two current publications (Eberhardt, 1977a, b).

Our further efforts along the lines of sampling for contaminants have included work on designing improved sampling plans for use at the Nevada Test Site and in DBER-sponsored studies of transuranic elements. This work is described in greater detail elsewhere in

this Annual Report. We prepared a paper concerning the sampling problems associated with the transuranic area (Eberhardt and Gilbert, 1978) and participated in a workshop held at Woods Hole in April 1977. We were involved in a second workshop dealing with sampling issues associated with contamination problems in "microcosm" research, in June 1977, sponsored by Oregon State University, NSF, and EPA.

We expect to continue our current emphasis on sampling for pattern in an effort to improve present methods used in appraising contamination as needed in determining current levels and planning remedial measures, if required, in various field situations. We also plan efforts to provide further designs for the application of the methodology of sampling for modeling to areas of DBER concern, inasmuch as it continues to be apparent that the evident advantages of "optimal" sampling schemes for designing, e.g., uptake and retention studies, seem not to be known to most researchers concerned with such problems.

Mechanisms for Animal Population Regulation

One of the key issues in evaluating the ecological effects of any human activity (such as energy development) is the ability of natural populations to compensate for various stresses. The important element in the ecosystem response is the population of a given species. The ability of populations to respond successfully to man-made insults is undoubtedly a consequence of the self-regulatory mechanism of the particular species. Since there has been a considerable argument as to the nature of these mechanisms for 30 yr or more ("density-dependence" vs "density-independence"), it will be apparent that the exact mechanisms are not known in precise detail. Enough is known, however, to make it evident that a current tendency to discuss energy effects in terms of the "health" of ecosystems is, generally, rather misleading. Prevalence of disease, or other evidence of the well-being of individuals, may be only one facet of the overall complex.

The major applied use of density-dependence as an operational expression of population self-regulation has been in fisheries research and management. In managing certain fisheries, empirical data on abundance are used in the form of a "stock-recruitment" curve. Two models for such curves have been generally in use, and are known as the "Ricker" and "Beverton and Holt" curves. We have reviewed the basis for these two models and found a connection that facilitates the choice of a model for a particular species-population (Eberhardt, 1977c).

Use of stock-recruitment curves depends on the accumulation of observational data extending over intervals measured in decades. When such data are not available, other approaches must be utilized. A number of criteria as to relative condition of a particular population may then be helpful, along with models for population dynamics. We have reviewed this approach for one group of mammalian species (Eberhardt and Siniff, 1977) and find that it may be useful in dealing with populations at or near maximal levels.

The ultimate goal in research on population regulation, and the consequent understanding of the ability of populations to compensate for human impacts, is necessarily a much-improved understanding of the basic regulatory processes. Full understanding will require many years, if progress along these lines in the last 40 or 50 yr is any guide. Much of the available data have been derived in the applied fields of entomology and fisheries management. Most of the species dealt with in those fields exhibit very high reproductive rates. It has seemed worthwhile to consider the accumulated evidence for species with much lower reproductive rates, i.e., the larger mammals. As a starting-place, we have formulated a generalized model for self-regulation in long-lived species. Starting with a population at a very low level of abundance (e.g., after introduction into a new, but suitable, habitat), the model predicts the following sequence of events as regulation develops:

$$\left\{\begin{matrix}\text{Immature}\\ \text{mortality}\\ \text{rates}\\ \text{change}\end{matrix}\right\} > \left\{\begin{matrix}\text{Age of}\\ \text{first}\\ \text{reproduction}\\ \text{shifts}\end{matrix}\right\} >$$

$$\left\{\begin{matrix}\text{Reproductive}\\ \text{rate of}\\ \text{adult females}\\ \text{changes}\end{matrix}\right\} > \left\{\begin{matrix}\text{Adult}\\ \text{mortality}\\ \text{rate}\\ \text{changes}\end{matrix}\right\}$$

Many details of the model remain to be evaluated. A particularly important feature in practical applications is whether or not the full sequence of events is required for regulation of a particular species-population. Our current views appear in Eberhardt (1977d).

Perhaps the most important outcome of our investigation is the emphasis on relative

position of the Maximum Sustainable Yield (MSY) point for long-lived species. The traditional model has been that of the logistic growth curve, for which MSY is at 50% of maximal levels. There is evidence that MSY may be appreciably below 50% for species with high reproductive rates (many species of fish and most insects). However, it now seems likely that many of the large mammals possess MSY points well above 50%. The most obvious implications of such a finding are: 1) optimal harvests are achieved near maximal populations, and 2) these species probably do not possess the same degree of "resilience" to environmental impacts shown by many other populations.

Transect Methods for Population Studies

Our work on transect methods has been continued this year with the preparation of a publication reporting findings subsequent to an earlier review. The focus of the earlier work was on line transects, in which all records of animals seen in the course of following a transect line are used, with auxiliary information on distances and directions, to estimate abundance. We have since broadened the scope of inquiry to include line intersects, for which the basis is interception of an object by a straight line, and modified strip transects, in which only animals or objects within a strip of predetermined width are utilized for census purposes.

The major current problems appear to be those associated with the line transect method as applied to censuses of inanimate objects, or to animals that do not exhibit a characteristic response to the observer's approach (e.g., by "flushing"). As mentioned in last year's Annual Report, we have been recommending a distribution-free method for application in such circumstances. For animals that flush, or otherwise definitely respond to the observer's approach, there is a "robust" method due to D. W. Hayne, with an appreciably smaller variance. Hayne's method is also nonparametric, in the sense that it does not depend on assumption of a particular curve of flushing-distances or sighting-distances. It is based on radial or sighting-distances. There is, however, a good deal of recent evidence that the method does not "work" for inanimate objects or animals that adopt a passive attitude to the observer. In these circumstances, it very likely will be necessary to use right-angle distances and to postulate a sighting curve or visibility curve. The distribution-free method mentioned above does not assume a specific curve, but instead uses, in effect, two "percentiles" of the observed distribution of right-angle distances.

In 1976, we cooperated in the design of a very large-scale line transect survey of porpoise conducted by the National Marine Fisheries Service (NOAA, Department of Commerce). Some five million nautical square miles were subsequently surveyed by two long-range aircraft and two NOAA research vessels. Initial examination of the data (currently under detailed analysis) suggests a further complication in that sighting probabilities appear to be strongly correlated with size of the porpoise school (ranging from single individuals to well over 1,000 animals). There is, thus, a need for further research on this feature, which makes nonparametric estimation questionable due to the small sample sizes available for many of the school sizes. Undoubtedly this phenomenon holds in most of the circumstances where groups of animals or objects are to be tallied. It has been studied for quadrat sampling but not for line transects (Cook and Martin, 1974).

Methods and Sample Sizes for Population Studies

One of the most frequently-asked questions concerning the design of ecological surveys is about sample size. Our efforts to provide some partial answers to that question have been summarized in a manuscript (Eberhardt, 1977e) and a summary of one segment of the data appeared in last year's Annual Report. In those instances where a specific objective for the study can be assumed, and a particular mathematical model postulated for the census method, a fairly specific answer can be provided for the sample-size question. The chief difficulty in these circumstances is usually that of justifying the assumptions on which the mathematical model rests. The weak point here is almost invariably the assumption that each animal in the population being censused has the same probability of inclusion in a sampling made at some particular stage in the census. Evidence that this assumption is often not tenable has been available for some time (cf. Seber, 1973).

In many circumstances, no effort is made to estimate the actual number of animals present on a study area. Instead, some relative measure of abundance is utilized. A variety of such indices are in regular use, based on diverse sources (visual and auditory contact, signs of various kinds, etc.). As a general rule, the process of

converting such indices to measures of absolute abundance ("censuses"), depends on the incorporation of some additional assumptions into a formal model, and perhaps on securing some additional observational data. Although rather widely used in practical management, indices tend to have a somewhat uncertain scientific reputation. Whether this is deserved or not very likely depends on the methods used in obtaining a particular index. When the data are carefully collected according to a well thought out and standardized sampling scheme, it may well be that the only significant difference between an index and a population estimate is that the investigator has been reluctant to invoke an assumption (such as the equal-probability-of-capture assumption mentioned above) that he knows to be faulty. In other cases, however, an index may simply represent haphazardly collected data that are not otherwise usable.

Since the chief problem in population estimation is closely associated with a widely collected and utilized, but seldom analyzed, kind of measurement of abundance, it has seemed to us that further research on the intersection of the two sets is in order. In the paper referenced above (Eberhardt, 1977e), we have assembled some models for indices and data on the relative variability (coefficients of variation) from a wide range of sources. However, time available and length of the present ms (80 typed pages) made it impossible to include an adequate treatment of indices per se. We have begun further research devoted to the analysis of indices and the question of the validity of the assumptions required for absolute measures of abundance.

Biostatistical Aspects of Impact Analysis

We have nearly completed our review of statistical methods that can be applied to actual data sets obtained at nuclear power plants. Our evaluation was designed to assess the advantages, disadvantages, and limitations of various quantitative techniques which we applied *a posteriori* to data sets (actual data analysis was funded by the Nuclear Regulatory Commission). We plan to use this experience so that we can offer methods applicable to impact assessment *a priori*. For such methods to be useful considerable attention to the conduct and design of field studies will be necessary.

We discussed (Annual Report, 1975) our experiences with the statistical analysis of data where the ratio of measurements (usually abundance) of concern at "impacted" sites relative to control sites was the variable. In addition the use of nested unbalanced and one-way analyses of variance were covered. Thomas (1977) discussed the limitations of analysis of covariance, regression, nonparametric methods, arithmetic differencing and simulation models. In Thomas et al. (ms submitted) actual examples of the applications of these methods to data collected at three nuclear power plants is presented.

Thus, we have investigated the various quantitative and qualitative methods we believe to be useful in assessing data from monitoring studies. From this experience we have been able to devise some estimates of sample size needed to detect statistically significant changes for lower trophic level organisms. Using those sample size estimates and one or more of the statistical analyses schemes we have suggested, as well as a field design based on the probable analysis procedure, it is very likely that changes in these biota, attributable to a power plant could be detected (if they exist). Thus, what has been done in environmental monitoring can apparently be done in a much more scientific manner resulting in statistically defensible assertions about lower trophic level biotic changes. These kinds of studies are not enough for most commercially important species because litigation has resulted in a requirement for an assessment of the affect of current insults on future populations. While such an assessment via simulation models may be possible, a quantitative assessment seems beyond the current state-of-the-art in ecology.

Since questions about effects on future (fish, shellfish, etc.) populations are being asked about projects ranging from nuclear power plants to dams and coal mines, and because monitoring data must be collected in an attempt to answer these questions, then a more useful plan for conducting environmental studies needs to be devised. We suggest such a procedure in Figure 7.1.

Projected population effects, about an order of magnitude below those which are considered ecologically detrimental, found year after year (for an agreed period of years) can form a stopping rule for monitoring studies for commercially important species. Thus, after T-years of model refinement and field studies, an impact estimate that is consistently an order of magnitude below an assumed ecologically detrimental level could constitute a point where field studies could be terminated. However, the estimates of key parameters used in the model must be obtained from well-designed field

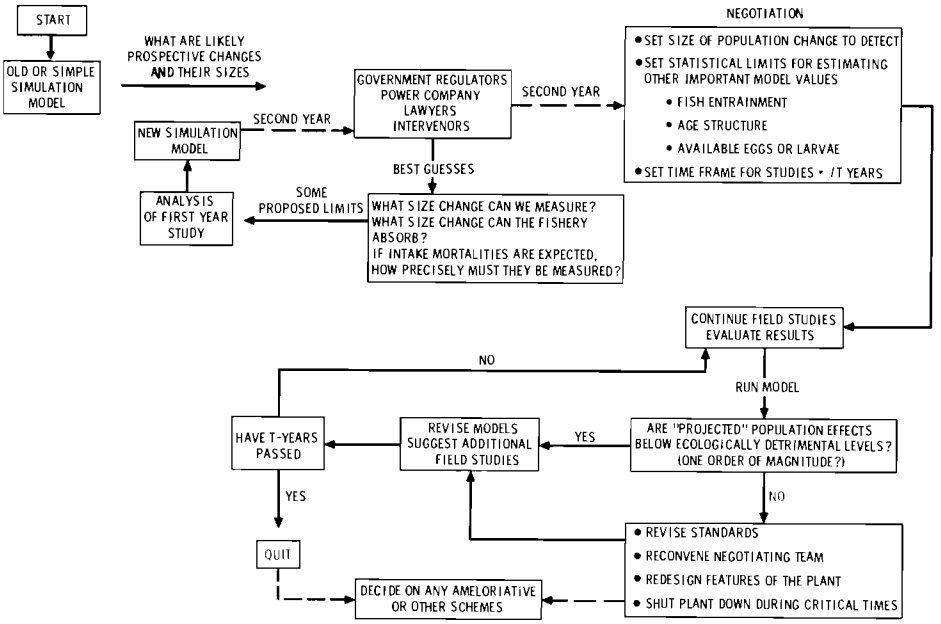

FIGURE 7.1. Plan for Conducting Environmental Studies of a Fishery at a Construction Site

studies conducted so that appropriate error estimates are obtained. These latter studies should be carefully designed and subsequently evaluated in terms of statistical precision (i.e., a fraction of available larvae entrained should be accompanied by a confidence interval and the study repeated several times during the part of the year when the particular species reproduces). Other parameters which are incorporated in models may include age structure and associated age specific mortalities, as well as estimated egg and larval losses from natural mortality. These estimates, as well as others, should be obtained as carefully and accurately as the state-of-the-art allows. Those field studies designed to estimate parameters that, when slightly changed, have a large effect on population "projections," should receive extra statistical design and analysis emphasis. Field studies conducted to determine some of the parameters above will be exceedingly difficult and the level of precision they can be expected to attain may be very low.

It should be stressed that answers to the question (What is the effect on future populations?) probably will not emanate from the program suggested in Figure 7.1 any more than from just sampling fish and shellfish, but some increased understanding both of fundamental ecology and better and more accurate simulation models should result in more accurate projections. Some benefits of the proposal outlined in Figure 7.1 include: 1) a stopping rule where after T-years of support of a good quality field monitoring program the applicant is allowed to terminate the studies, 2) a chance for some of the imaginative scientists currently doing routine monitoring to design and carry out field studies which address key questions in population ecology, and 3) the opportunity for both statisticians and simulation modelers to institute and/or direct (or at least suggest directions for) portions of field work.

Since field monitoring programs were instituted under the mandate to assess impact called for by NEPA in 1969 little, if any, progress has been made toward addressing the crucial population effect issue. The proposal outlined in Figure 7.1 should bring us closer to that goal in the future than the continuation of monitoring studies as now conducted.

Similarity Analyses

With the availability of additional data we have again focused our attention on this research topic (1975 Annual Report). When we incorporated this additional data, we found that the linear relationships we formerly proposed may, in fact, be nonlinear (residual MS of linear and logistic fits are 39 and 8,

respectively). However, if the analysis is conducted by "class of element" (e.g., transition metals, alkaline earths, etc.) it appears that more than one linear relationship may be present.

In a separate development it was brought to our attention that the expression for average half-time is mathematically related to biological equilibrium level (Dr. Charles Mays, personal communication).

This latter variable is calculated using the entire exponential retention function (calculated from whole body counting data after a single oral ingestion of a radionuclide). Preliminary research using average biological half-time (which also is based on the entire exponential retention function) gave results similar to those obtained using biological equilibrium level. We have previously been discouraged by the poor similarity ratios obtained using long-component biological half-time (mostly because interspecies predictions of half times for ecosystem models was the original impetus for the research). Our current results using average half-time, while not definitive, are encouraging, and we are preparing a ms for journal submission.

We believe we have shown that the ideas of similarity analysis appear to be promising both as a method to extrapolate metabolic data among nonruminant species (including man) but also as a device to determine biological half-times for ecosystem analysis. While some complex statistical questions are as yet unresolved, we are led to speculate that similarity ratios for other classes of compounds may be useful.

Marine Mammal Studies

As remarked in last year's Annual Report, we have been cooperating in a variety of marine mammal studies. Origins of our involvement are varied, including field work with Antarctic species some years ago and, more recently, appointment of L. L. Eberhardt to the Scientific Advisory Committee of the U.S. Marine Mammal Commission. Relevance to energy development activities is both direct (oil and mineral exploration, development, and transport; "bioconversion" techniques, etc.) and indirect (models for impacts of human activities on natural populations).

An important aspect of the Marine Mammal Commission work stems from the fact that the enabling legislation, the Marine Mammal Protection Act of 1972, constitutes a pioneering attempt to institute ecosystem management by legislative mandate. In the Act, it is made clear that the intent of Congress is to institute management policies directed towards maintaining "optimum sustainable population" (OSP) levels. Unfortunately, a precise definition of OSP and related terms is not available, so a good deal of effort has been devoted to attempts to achieve working definitions. As time goes on, such definitions attain legal status (through publication in the Federal Register), and become precedents for further legislation. There are, thus, strong reasons for careful attention in these formative stages. Some further details of the problems involved for marine mammals appear in Eberhardt (1977f) and, somewhat more generally, in Eberhardt (1977g).

Our work with Antarctic seals has been summarized in a recent publication Siniff et al. (1977a) and has been extended to a broader consideration of problems in the conservation of polar marine mammals Siniff et al. (1977b). The latter publication includes consideration of research, management, and impacts of economic development. An important distinction exists between the northern polar regions, in which resource exploitation of various kinds has been underway for some time, and the southern regions. In the south, the only past exploitation has been directed towards some of the marine mammals (whales, fur seals, elephant seals), but the prospect of mineral exploitation is now surfacing.

Nonlinear Regression for Ecological Data

As a part of a project to evaluate simulation models we have begun to collect available computer programs which estimate parameters in nonlinear regression models. Several new programs have been received and an extensive bibliography collected. In addition, we have extensively reviewed a code written at Hanford (Learn-Likely) with the aid of Dr. P. Doctor of the Energy Systems Department. Because most such codes are run in a batch mode (usually several times before a satisfactory fit or failure to fit results) and each run is fairly expensive, we have developed an interactive BASIC code (COMP) which runs on both a PDP 11/70 or PDP 11/34 computer. This circumvents both the considerable turnaround time for batch systems and costs/run are extremely low on such minicomputers. Resulting parameter estimates can be used as guesstimates for more precise (double precision accuracy) maxi-computer

codes and to obtain a full suite of statistical results and any diagnostic statements which are printed during the fitting process (suggesting erroneous fits).

The program uses the linearizing or Taylor Series expansion of partial derivatives. Therefore, partial derivatives must be supplied (as well as the function) by the user for any new models not currently contained in the programs. It should be noted that when a linearizing method is used to estimate parameters in a nonlinear model, all the usual procedures of linear regression theory can be applied. However, the results so obtained are only valid insofar as the linearized form approximates the true model.

The output of COMP includes the variance-covariance matrix, t-tests for parameters, Von Neumann's ratio, observed, predicted and residual values, the error mean square, and an optional procedure to evaluate heteroscedasticity. In the latter procedure the absolute values of the residuals are fit using a linear regression model. Thus, deviations which are significantly larger as X increases (usually X is time) may be detected using the linear regression. One explanation for such behavior may be multiplicative rather than additive errors.

The key to the system is the reenterant nature of the curve fitting routine (allowed only with an interpreted language such as BASIC). In general, the user supplies estimates of the parameters for selected model (18 are currently available). The program calculates a requested number of iterative refinements (hopefully improvements) to the parameter estimates in an attempt to minimize the squared deviations between the values predicted by the model and the observed data. During program execution the user can observe whether the results are logical. If not, the process may be stopped, new parameter estimates tried, the current fit examined, the process of iteration started again, or a new model selected. A detailed user's guide for running COMP on the PDP 11/34 and 11/70 has been prepared (Thomas et al., 1977). In addition, we will present our results at the fall DECUS U.S. Symposium to be held in San Diego, California, 29 November - 1 December 1977.

Other Activities

As in the past, a substantial amount of effort has been devoted to consulting and similar technical services to other projects and to a variety of program and project reviews. These include several proposal reviews for DBER, reviews of a number of manuscripts as requested by journal editors, and two published book reviews.

Participation on an ICRP panel (Thomas) continued this year, and a substantial effort was devoted to reviewing a proposed EPA document on plutonium contamination in soils, as well as to consulting on various soil sampling problems locally and at other sites. Several conferences and workshops were attended, both as part of our own program efforts, and to assist other projects in Ecosystems Department.

Our involvement in academic affairs has included various kinds of cooperation with several universities. Dr. Thomas has been serving as a coordinator for a Master's program in biology at the Joint Center for Graduate Study (Richland) and has been appointed as an Adjunct Associate Professor at Washington State University. Dr. Eberhardt continues as Affiliate Professor at the University of Washington.

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• Effects of Water Quality Alterations on Fish Behavior

Principal Investigators: R. H. Gray and J. M. Haynes

Objectives of this project were to study behavioral patterns of ecologically or economically important fish. To minimize potential effects, data on fish behavior are essential for proper design and operation of thermal and chemical outfall and water intake structures. The work is applicable to nuclear, fossil fuel and hydroelectric generating plants.

Pressure-sensitive radiofrequency transmitters were used to monitor behavior of returning adult chinook salmon in relation to gas supersaturated water on the lower Snake River. During fall and spring 1977, 40 fish were monitored between the river mouth and the fourth upstream dam. Equal numbers of fish served as controls. Results indicated swimming depths were significantly shallower in normally saturated water than the previous year in water supersaturated with atmospheric gases.

White sturgeon previously tagged with radio transmitters were monitored to study location, seasonal movement, and behavior of a valued species in a section of the Columbia River influenced by two hydroelectric dams and thermal loading from a nuclear power plant. Additional sturgeon were tagged with temperature-sensitive transmitters and monitored to evaluate thermal preference. Results indicated all size classes preferred free-flowing areas of the river and were relatively inactive in winter. Most movement occurred in summer. Diurnal variations in environmental temperatures and positions of sturgeon tagged with temperature-sensitive transmitters indicated movement into shallow shoreline areas at night.

Data on the instantaneous response of juvenile chinook salmon encountering a simulated river thermal plume interface were published in the open literature and presented and discussed at two symposia.

Depth Distribution of Chinook Salmon in Relation to Gas Supersaturated Water

Studies to monitor behavior of returning adult chinook salmon (Oncorhynchus tshawytscha) in relation to gas supersatured water in the Snake River continued in FY-77. Procedures and rational for the study were detailed in previous Annual Reports. Previous results had indicated fish spent more than 85% of their time below the critical supersaturation zone during a high runoff year.

FY-77 efforts evaluated swimming depths of chinook salmon in the absence of supersaturated water. During fall 1976, with gas saturation values of 101%, 9 fish carried internal pressure-sensitive radio transmitters and metal core anchor tags. Ten control

fish carried only metal core anchor tags. Comparison of travel times and percent passage at upstream dams supported previous conclusions that internal tagging affected upstream movement. Thus, external tags were used in spring 1977. In spring 1977, with gas saturation values of 107%, 30 fish had external pressure transmitters and anchor tags. Additionally, an equal number of fish were anchor tagged only as controls.

Swimming depths of fall 1976 and spring 1977 chinook salmon were shallower (Table 7.3) than those of spring 1976 fish, and the differences were significant ($p<0.05$). Our in situ studies showed adult chinook salmon swam deeper in supersaturated water than in normally saturated water and, thus, avoided potentially lethal conditions. In all cases, mean depth of travel was below the critical zone.

TABLE 7.3. Depth Distribution of Chinook Salmon Tagged Externally or Internally with Pressure Sensitive Radio Transmitters in the Snake River

	Percent Time at Depth			
	Spring 1976[a]		Fall 1976[b]	Spring 1977[c]
Depth, m	External Tags	Internal Tags	Internal Tags	External Tags
0-1	2.9	2.4	22.5	10.9
1-2	7.4	9.4	13.2	19.8
2-3	12.0	17.1	21.2	18.3
3-4	7.1	12.3	9.9	13.4
4-5	21.1	10.8	13.9	9.8
5-6	10.2	11.3	7.9	8.3
6-7	6.5	4.3	4.0	6.0
7-8	4.9	4.2	4.6	4.0
8-9	9.5	7.6	2.0	3.0
9-10	7.1	2.3	0.7	2.8
10-11	5.1	2.8	0.0	1.3
11-12	4.3	4.6	0.0	0.8
12-13	0.6	8.9	0.0	0.8
>13	1.1	1.9	0.0	0.9
Number of Fish	12	14	9	30
Number of Depth Recordings	1444	1246	151	2761
Mean Depth	5.7	5.8	3.1	3.8

[a] Atmospheric Gas Saturation in the Snake River ranged from 124-129%

[b] Atmospheric Gas Saturation in the Snake River was about 101%

[c] Atmospheric Gas Saturation in the Snake River ranged from 106-107%

Results of this work have been published in the open literature, submitted for publication, reported at scientific meetings and will appear in a doctoral dissertation. Additional manuscripts are in preparation.

Seasonal Location, Distribution and Movement of White Sturgeon in the Hanford Reach of the Columbia River

Studies to monitor seasonal location, distribution and movement of white sturgeon (Acipenser transmontanus) in the Hanford Reach of the Columbia River continued in FY-77. Procedures and rationale for this study were detailed in last year's Annual Report. This year, additional fish were instrumented with radio transmitters yielding information on position and 12 sturgeon were tagged with temperature sensitive transmitters to evaluate thermal preference in this section of the Columbia River. Monitoring of these and previously instrumented sturgeon occurred in FY-77 and will continue for the duration of transmitter life. Results indicate all size classes prefer free-flowing areas of the river and are relatively inactive in winter. Most movement occurs in summer. Preliminary temperature data show a diurnal cycle and suggest sturgeon spend the evening in shallow, warmer shoreline areas possibly to feed.

Results of this work have been submitted for open literature publication and will appear in a doctoral dissertation. Additional manuscripts are in preparation.

Initial Response of Juvenile Chinook Salmon to a Simulated River Thermal Plume Interface

Experiments to evaluate initial responses of juvenile chinook salmon (Oncorhynchus tshawytscha) to simulated thermal effluent were terminated at the end of FY-76 and results given in last year's Annual Report. Efforts continued in FY-77 to publish and discuss the implications of project results in the open literature and two symposia.

- **Ecological Effects of Combined Aquatic Stressors**

Principal Investigators: D. R. Anderson, C. D. Becker and M. J. Schneider

Technical Assistance: S. A. Barraclough and M. L. Wolford

The title of this program represents two major research areas formally separate projects, now combined under one title. This combination represents a recognition of the close relationship of the information each is generating. The program titles formerly used were: "Effects of Thermal Discharges on Aquatic Biota" and "Combined Effects of Waste Heat and Environmental Factors Acting in Concert."

The former was designed to measure thermal injury, latent and manifest, in fish and other organisms important in aquatic food chains. The latter makes use of such thermal data to determine when and how multiple pollutants, including thermal increments, affect fish. A key concept emerging from these studies is that of multiple stressors; i.e., where several pollutants each, at "sublethal" concentrations, act together to cause significant abnormality or death. This is probably the typical situation where environmental impact becomes manifest.

The major effort in the former project area has been the publication of information gathered to date. One paper has been published this year, one submitted, and a third is undergoing review. A hypothesis which could delineate the stamina limitation of fish under various sublethal stress is currently being tested.

In the latter project, the studies of combined effects of multiple chemical and thermal parameters, in a single bioassay, represent a relatively new area of research. One of the very interesting findings in this research is a heightened toxicity of Ni caused by rather low concentrations of chlorine. Work is based on flow-through bioassays, using multiple temperatures and chemical species. Rainbow trout, Salmo gairdneri, and coho salmon, Oncorhynchus kisutch, were assayed. During the next phase of the program, sublethal parameters such as growth, bioaccumulation and tissue destruction will be measured in response to the low level, sublethal toxicant dosages.

Effects of Water Temperature on Excercise, Blood Glucose and Lactate of Rainbow Trout

A variety of environmental factors are known to influence the metabolic activity of fish and, therefore, their response to stress. Two of the more important factors are water temperature and the level of fish activity. The purpose of this study is to investigate the interrelationships of fatigue and water temperature on fish tolerance to stress. This project assesses the combined effect of induced swimming and exposure to thermal stress on the performance ability of fish and physiological parameters, blood lactate and glucose.

The major effort of the past year has been the publication of the large volume of information developed by the research efforts to date. A paper entitled "Trap Tank for Nontraumatic Serial Sampling of Fish Stocks in Physiological Studies" was published in the July 1977 issue of the Progressive Fish Culturist.

The construction details of a device which allows unbiased sampling of fish for physiological studies are described. The device consists of two rectangular tanks, connected by a tunnel, which contain a trap door in the floor. A single fish swimming through the tunnel can be removed by opening the trap door; the tunnel is isolated from the two tanks by flap-valve doors when the trap door opens. Blood glucose and lactate levels of fish serially removed from the tank remain stable throughout the sampling day.

A second paper entitled "Effects of Water Temperature and Exercise of Fish Energy Metabolism" has been submitted for publication and is currently undergoing review. This paper discusses the combined effect of acute sublethal heat stress and enforced swimming acting in concert. Rainbow trout, Salmo gairdneri, acclimated to 12°C were exposed to 12, 17, 22 and 27°C while simultaneously responding to two levels of exercise, static (no swimming) and swimming at cruising speed. Measurements of blood glucose and lactate levels were taken at the end of a 30 min swimming period. The blood glucose levels at 12 and 17°C appear unaffected by temperature; at 22 and 27°C the glucose elevation is significant. A similar pattern was seen in the lactate determinations with significant elevation occuring only at 27°C. An interaction of exercise and temperature was found in the blood glucose and in the performance of the trout. It is hypothesized that the failure of trout to complete the exercise-temperature regimen may be due to the development of tissue hypoxia rather than the buildup of blood lactate.

The affect of temperature acclimation on the blood chemistry parameters, glucose and lactate, are discussed in a third paper. This manuscript has been drafted and is currently undergoing review by appropriate PNL staff. We anticipate submittal of the manuscript before the end of the calendar year.

An important hypothesis was developed during the analysis of the data discussed in the second paper (abstracted above). The development of this hypothesis is a significant point of progress because if verified, it will explain the physiological basis for failure of fish stamina under combined stress of swimming and elevated temperature. This information would provide the necessary data base to substantiate engineering decisions regarding allowable discharge temperatures in flowing waters. It is the testing of this hypothesis that we will next address. Should the hypothesis prove correct, it will be useful to the understanding of fish performance capability under physiological stress, particularly stressors other than temperature and exercise which interfere with oxygen uptake and transfer, e.g., chemical toxicants.

The Combined Effects of Nickel, Chlorine and Temperature on Rainbow Trout and Coho Salmon

The combined effects program is designed to quantify the combined action of thermal stress and two chemical pollutants, nickel and chlorine, on the physiology of rainbow trout, Salmo gairdneri, and coho salmon, Oncorhynchus kisutch. These chemicals were selected because of chlorine's use as a biocide and the use of nickel in a large percentage of the types of condenser tubing in steam electric stations. The affect of temperature on the toxicity of these two components is being studied due to the thermal component normally associated with effluents from steam electric stations.

The use of the combined effects approach is estimating the toxicity of multiple chemical and thermal parameters in a more realistic approach than a single factor approach in estimating the actual toxicity of effluents which contain multiple toxicants. The objective of the program is to study the interactions and mechanism of toxic action of nickel and chlorine at several water temperatures on coho salmon and rainbow trout. Acute flow-through bioassays are underway in a modified Mount-Brungs proportional dilluter.

Sublethal parameters of growth, bioaccumulation and tissue destruction are being measured in response to low-level toxicant dosage. A factorial experimental design including three levels of chlorine and three levels of nickel at different temperatures is being used. This enables statistical evaluation of each effect and the interaction of the combined effect of the toxicants and temperature. Both 96-hr (4 day) and 336-hr (14 day) bioassays are being conducted. Samples of gill, liver, and muscle tissues are being taken to monitor bioaccumulation of nickel tissue destruction.

A synergistic effect of chlorine and nickel toxicity on rainbow trout has been demonstrated. Concentrations of 0.05 ppm, Total Residual Chlorine (TRCl) result in fish mortality of 5%. Nickel concentrations ranging from 4 to 8.5 ppm result in 0% mortality. When these levels are combined the resultant mortality ranges from 95-100% of the fish exposed during a 96-hr bioassay. This is the first incidence reported in the literature of a chlorine-nickel synergistic toxic effect.

Evaluation of the "Critical Thermal Maximum"

Experiments were completed in FY-77 to critically evaluate the effects of increasing water temperatures at different rates on Critical Thermal Maximum (CTM) determinations by using representative warmwater and coldwater species of fish.

Rationale and results with pumpkinseed sunfish (Lepomis gibbosus), were presented in the previous Annual Report. Results with fingerling coho salmon (Oncorhynchus kisutch), data analysis, and potential applications of CTM data are summed here.

The CTM is a parameter used to determine the thermal resistance of cold blooded organisms by increasing (or decreasing) the temperature at a constant rate. The point where "locomotor" activity becomes disorganized and the animal loses its ability to escape from conditions that promptly lead to its death is the CTM.

Since various investigators have used different rates of temperature change to determine CTM's of fish, results are not strictly comparable. Standardization of methods is particularly important when the CTM is used to quantify sublethal effects on fish exposed to environmental stresses. We are concerned, in other phases of our program, with potential chemical contaminants derived from development and utilization of coal, tars, and oil shale as energy sources.

In our studies with juvenile coho salmon (a coldwater species), acclimations were at 5 and 15°C rather than at 10 and 20°C as used for pumpkinseed sunfish (a warmwater species). Other conditions were identical. Controlled temperature increases were 1, 6, 18, 30 and 60°C/hr. The data obtained were time and temperature of loss of equilibrium (LE) and death (D). Multiple comparisons of the derived CTM means were made to aid in evaluating temperature increase rates, Table 7.4.

TABLE 7.4. Comparison of CTM Means for Juvenile Coho Salmon by Duncan's New Multiple Range Test[a]

Acclimation Temperature	Endpoint	CTM Means at Indicated Heating Rate				
		1°C/hr	6°C/hr	18°C/hr	30°C/hr	60°C/hr
5°C	Loss of Equilibrium	25.01	24.84	25.32	25.87	25.80
	Death	25.65	26.09	27.51	28.18	29.16
15°C	Loss of Equilibrium	27.22	28.13	28.70	29.16	29.63
	Death	27.56	28.75	29.72	30.05	31.15

[a]Any means not underscored by the same line are significantly different at the 0.05 level of significance

LE temperature means for fish acclimated at 5°C were not significantly different at heating rates of 1, 6 and 18°C/hr, nor were the 30 and 60°C/hr rates significantly different from each other. But the 1, 6 and 18°C/hr heating rates differed significantly from the 30 and 60°C/hr rates. LE temperature means for fish acclimated at 15°C were all significantly different from each other.

D temperature means for fish acclimated at 5°C were all significantly different from each other irrespective of heating rate; the same is true for fish acclimated at 15°C. This assessment confirms that standardization of methods used in CTM determinations is required.

• Effects of Energy Systems Effluents on Coastal Ecosystems

Principal Investigators: G. Roesijadi and J. S. Young

The primary concern of this program is to determine the effects of potential toxicants resulting from energy technologies. This information is needed to: 1) assess the need for further study on the bioavailability and cycling of the contaminant, 2) provide a defined endpoint by which bioavailability can be measured, 3) determine the lowest concentrations that can be safely released into the environment to allow for minimal impact and maximum use of our resources, and 4) describe the effects that are manifested and how they contribute to an ecosystem. During the past year, work has centered on the two major chemical contaminants, chlorine and copper, released by the operation of cooling systems.

Chlorine

The studies on the effects of seawater chlorination on marine animals to date have primarily been concerned with the relative sensitivities of a number of Pacific Northwest marine species to total residual oxidants (TRO). The species we have tested had a wide range of sensitivity, with 96-hr LC_{50} values ranging from 0.032-1.418 mg/ℓ TRO (Table 7.5). Ontogenetic effects have also been identified in related studies. For example, morphological deformities were observed in juvenile shiner perch exposed to TRO, and exposure to TRO delayed hatching of coon stripe shrimp eggs.

In order to understand the reason for this wide variation in sensitivity and the mechanisms involved in producing adverse effects, research has been initiated to examine the physiological responses of organisms exposed to chlorinated seawater. Integrated with these research studies are the identification of biologically active compounds produced by seawater chlorination.

Existing data indicate that the presence of TRO is disruptive to the normal function of major physiological systems, particularly those associated with gas and ion transport such as gills and blood. To date, most of

TABLE 7.5. The Relative Sensitivity of 15 Fishes and Invertebrates to Chlorinated Seawater as Indicated by 96-hr LC50 Values

Name [a]	Number of Valid Tests	96-hr LC50, mg/ℓ TRO	95% Fiducial Limits, mg/ℓ TRO	Probit Regression Line Slope
Coho salmon, j [b] *Oncorhynchus kisutch*	3	0.032	0.026-0.038	21.2
Chinook salmon, j *Oncorhynchus tshawytscha*	2	- [c]	-	-
Pink salmon, j *Oncorhynchus gorbuscha*	3	-	-	-
Pacific Herring, j *Clupea harengus*	2	0.065	0.033-0.097	14.7
Shiner perch, j & a *Cymatogaster aggregata*	5	0.071	0.045-0.098	23.5
English sole, j *Parophyrys vetulus*	3	0.073	0.044-0.103	10.3
Pacific sand lance, j & a *Ammodytes hexapterus*	6	0.082	0.062-0.102	21.9
Shrimp, a *Pandalus goniurus*	3	0.090	0.063-0.119	27.8
Shrimp, a *Crangon nigricauda*	6	0.134	0.118-0.151	17.0
Amphipod, a *Anonyx* sp.	4	0.145	0.118-0.173	12.8
Nysid, a *Neomysis* sp.	4	0.162	0.150-0.175	14.1
Threespine stickleback, j & a *Gasterosteus aculeatus*	3	0.167	0.141-0.193	21.6
Coon stripe shrimp, j & a *Pandalus danae*	4	0.178	0.159-0.199	19.0
Amphipod, j *Pontogeneia* sp.	5	0.687	0.583-0.864	27.0
Shore crab, j & a *Hemigrapsus nudus* and *H. Oregonensis*	5	1.418	1.240-1.530	14.2

[a] Identified using keys in Hart and Kozloff.
[b] j = juvenile, a = adults
[c] The low number of data points between 0 and 100% mortality prevented calculating LC50 values for chinook and pink salmon. The mortality data obtained indicated sensitivity close to the coho and greater than the Pacific herring.

the research along these lines has been confined to freshwater systems. These studies examine the effects of seawater chlorination and specific compounds resulting from chlorination activities. Studies have been initiated on the affects of chlorinated seawater on ionic/osmoregulatory and respiratory physiology of selected marine invertebrates.

Currently, the relationship between ammonia excretion and exposure to chlorinated seawater in a marine crustacean, Cancer productus, the red rock crab is being investigated. Other work has demonstrated that some compounds created from the chlorination process (particularly chloramine and bromamines) can be harmful to marine organisms. These latter compounds result from the reaction of chlorine and bromine with ammonia. Since ammonia is an excretory product of aquatic animals, it is possible that microenvironments may exist in the region of ammonia excreting organs, such as gills, in which halomines (formed by reactions with ammonia and chlorinated seawater) may be present in relatively high concentrations. At the present time, the relationship between ammonia excretion and exposure to chlorinated seawater is being studied. Studies to identify halogenated organic compounds formed as a result of seawater chlorination, under sponsorship of the Nuclear Regulatory Commission, are being closely integrated with these effects studies.

Copper

The primary concern about a bioavailable contaminant is whether it may cause an adverse effect to a marine organism. If it does, then the next step is to assess the potential population and community level response that will result from the individual effect. At this time, these studies are concentrated on the individual response to elevated copper levels with two organisms, Eudistylia vancouveri and Pandalus danae. These organisms have been chosen as representatives of two physiological types; those that do not have a copper based respiratory pigment, and those that have Cu^{++} in the transport of oxygen.

Eudistylia vancouveri, a sedentary tube dweller with an anterior display of pinnate gills, is found in coarse sediments or attached to local pilings. To date, we have determined the following: 1) background tissue levels of copper range from 3 to 9 µg/g in the body and 5 to 18 µg/g in the gills; 2) copper begins to accumulate in tissues upon exposure to concentrations between 3 and 6 µg/ℓ Cu^{++} (Figure 7.2); 3) gills accumulate more copper than does the body; 4) at increasing concentrations of copper, chemical injury is manifested by corresponding increases in gill necrosis and autotomy; and 5) E. vancouveri withdraws into its tube more frequently upon exposure to copper.

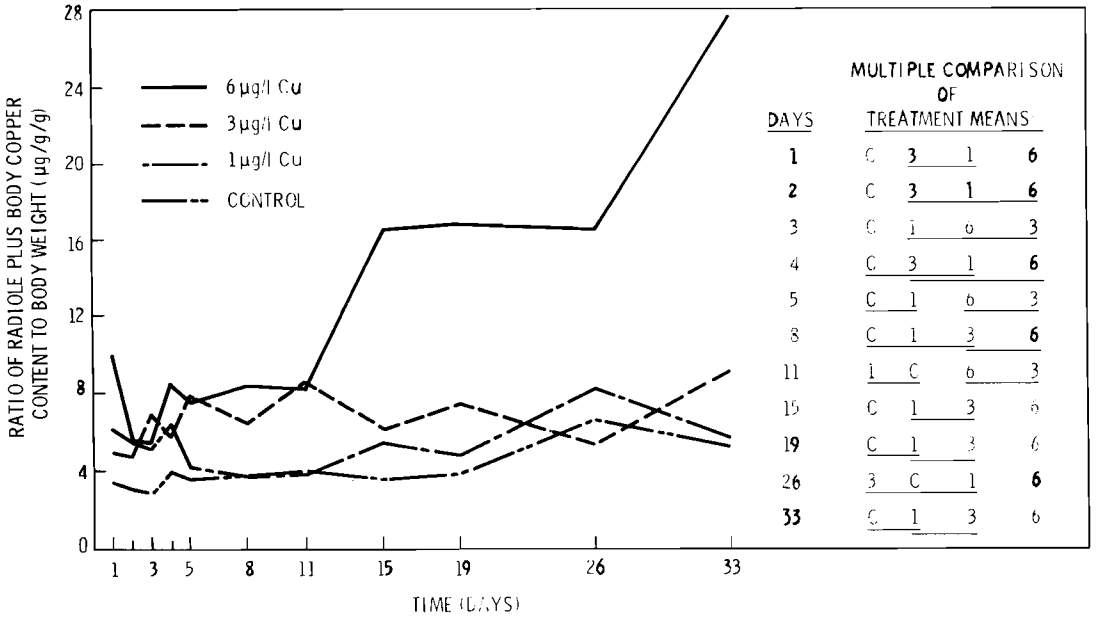

FIGURE 7.2. Ratio of the Sum of Gill and Body Copper Contents to Body Weight After Exposure to Copper - Means and Their Multiple Comparisons Over Time

A major task in FY-78 is to determine a threshold copper level for gill injury in Eudistylia, copper uptake rates and accumulation as injury progresses, its histopathology, and probably its ultrastructural characteristics. The last will help define the toxic mechanism. Evidence indicates cell membrane breakdown and lysosome rupture. In time, this will be compared to ultrastructure of gill injury in Pandalus.

Other tasks include the examination of the behavioral response to copper in Eudistylia and 1 yr exposure of Eudistylia at low level copper to examine long-term accumulation and chemical injury. Under winter conditions Eudistylia begins to accumulate increasing copper with time, at a concentration between 3 and 6 µg/ℓ Cu^{++}. It is essential to determine whether a steady state will occur with time or whether body levels will continue to increase. The tissue level responses such as gill necrosis will also be examined, along with the organisms ability to avoid exposure via behavioral responses.

For the copper regulator Pandalus, the following have been established: 1) the 96-hr LC_{50} for Cu^{++} is 72 µg/ℓ; 2) all tissues examined, except muscle, accumulate copper. Gills and the hepatopancreas gain the highest levels during a given exposure period; 3) the level of copper accumulated in tissues increases with its exposure concentration; 4) this response (Figure 7.3) has been described histologically along with an inflammatory response. Gill necrosis developed in one week at 50 µg/ℓ Cu^{++}; 5) necrotized gill tissue upon elimination of the moult is not regenerated with continued exposure to copper.

Since Pandalus is mobile and it may move in and out of copper contaminated areas studies are underway to determine how well it can recover by examining copper accumulation and depuration. Research completed this past year indicates that depuration is rapid in all tissues except the hepatopancreas, and that a major release mechanism is through the moult. Studies in FY-78 will look at other tissue level responses to determine their role in the movement and accumulation of copper in Pandalus. Pandalus larvae developed through all stages at 10 µg/ℓ Cu^{++}, but not at 20 µg/ℓ. Experiments are planned to define the threshold for these larvae since larvae of many aquatic animals have been shown to be more sensitive to toxicants than adults.

FIGURE 7.3. (A) Section of Gill from Control Shrimp; MV = marginal vessel, EC = epithelial cell, PC = pillar cell. (B) Section of Gill from Shrimp Exposed to 20 ppb Cu, Showing Affected Lamellae Adjacent to Normal Appearing Lamellae; H = hemocytes, N = necrosis. (C) Section of Affected Gill Showing Extensive Hemocyte Infiltration.

• Bioavailability of Energy Effluent Materials in Coastal Ecosystems

Principal Investigators: E. A. Crecelius, C. I. Gibson, L. D. Kannberg, J. E. Rogers, R. L. Schmidt, J. S. Young, K. H. Abel, and D. E. Robertson

The bioavailability program is engaged in research to provide an understanding of the processes involved in the cycling of materials resulting from energy technologies in the marine coastal ecosystem. The primary goal of the program is to define the fate and ultimate ecological consequences of energy technology-produced materials in the coastal ecosystem.

One of the major problems limiting the ability to predict the effects of a contaminant in the marine environment is the inability to equate an analytically-defined fraction of the total amount of material in the environment with a biological response. This problem is particularly limiting for long-term effects where chemical modification is likely to occur because of chemical, physical and biological influences. The bioavailability program has begun a number of tasks to solve this problem and provide an understanding of the processes and mechanisms that control the bioavailability and cycling of materials in the coastal ecosystem.

This year, our work was concerned with: 1) the chemical forms and quantities of radionuclides being released by a nuclear-fueled steam electric station, 2) the chemical form and reactions of copper, 3) the biological uptake of a specific form of copper over long periods of time, 4) the reaction of Cl_2 in seawater and its resulting compounds, 5) the sediment-water interactions of metals in natural and altered systems, and, 6) the development of a model capable of including physical, chemical; and biological interactions in predicting the dispersion of contaminants from a point or multiple sources.

Radionuclide Studies

Physicochemical characterization studies of aqueous process streams at San Onofre Generating Station Unit #1 were conducted to provide source term information concerning the forms of radionuclides being released into the marine environment. This information is needed for future field sampling efforts and laboratory studies of the bioavailability of these materials.

Sampling was conducted on the primary coolant, secondary steam condensate, processed low level wastes and tertiary coolant at several different times in the nuclear fuel cycle. Radionuclides were partitioned into particulate, cationic, anionic, and nonionic species in the reactor process streams, and into particulate and soluble species in the tertiary seawater coolant. Characterization of the particulate species included a detailed size distribution. No measurable radioactivity was found upon examination by a large volume concentration technique of secondary steam condensate. Similarly, no observable activity was found in the tertiary coolant during normal operations when the

reactor was not discharging low level waste. Both of these samples indicate negligible cross-leakage between coolant loops.

Examination of low-level waste immediately prior to release has indicated extremely variable radionuclide compositon and variable and sometimes unexpected physicochemical forms in the waste. Predominant γ emitting nuclides in the low level waste are ^{57,58}, ^{60}Co, ^{110m}Ag, ^{134,137}Cs and ^{124,125}Sb. Detailed examination of particulate material in the low level waste has shown the presence of a wide spectrum of particulates in the low level waste and also significant variability in the particle size spectrum during a release.

An investigation at San Onofre Nuclear Generating Station included evaluation of the efficiency of our in-plant water sampler for soluble species. Sampler efficiency for ionic species was evaluated through the use of multiple resin beds. Cation removal was demonstrated to be quantitative in the first resin bed for all cationic species. Anion removal was less efficient and ranged from 85% for cobalt species (^{58}Co, ^{60}Co), to 75% for ^{124}Sb and ^{125}Sb.

Large volume water sampling conducted at the tertiary coolant outfall has shown detectable radioactivity during low-level releases. Preliminary measurement and mass balance indicate either: 1) incomplete mixing at our sampling point with rapid adsorption to particulate matter present in seawater, or 2) less rapid phase redistribution upon release, but a gradual increase in particulate-associated radioactivity in the area of the outfall.

Further studies are underway to examine the release of radionuclides from the particulate phase and the behavior of soluble rad waste upon mixing with seawater. The results of these studies will give insight into environmental behavior after release of the low-level waste to the marine system and further elucidate the processes occurring in the outfall.

Copper Studies

Copper is a product of energy-related effluents that enter the marine ecosystem. The recent refinement by us and others of the use of Anodic Stripping Voltammetry (ASV), an electrochemical analysis to measure and characterize copper in its dissolved chemical forms, has enabled us to further define the form of copper existing in natural systems and monitor our controlled systems. For example, we have found by ASV that "clean" Pacific Northwest marine waters contain from 0.04 to 0.40 µg/ℓ total copper. Waters near the Seattle industrial complexes contained 1.4 µg/ℓ. Little of the copper is in the ionic (Cu^{++}) form; most is complexed with other molecules. The seawater used in our laboratory has an excess complexing capacity of between 10 and 20 µg Cu/ℓ, depending on season and other water conditions.

The relationship of electrochemically measured copper forms and their availability to marine organisms was investigated to determine how the complexation capacity of the seawater influences copper uptake. This information is needed to assess and predict the effects of metals from energy-related effluents. Copper is a micronutrient that is accumulated by organisms, but regulated at a constant body level. However, above a certain threshold concentration, copper accumulation increases with time, provided the metal is in an available form. In general, the literature has not identified the form of copper that is responsible for measured effects. When a seawater/copper solution is not aged, accumulation is greater than if it is aged, which indicates a change in the copper form, probably from an ionic form to a complexed one. The bonding of weakly-complexed copper may be broken by an organism to make it available or may act as a copper carrier. The objective is to define these relationships, understand some of the mechanisms of metal bioavailability and, thereby, be better able to produce long-term consequences of such ions in energy effluents.

Chlorine Studies

A number of experiments were conducted to determine the relationship of our measurements of total residual oxidants (TRO) in seawater to those being made by researchers at other sites. The results of these investigations are that the developed procedure for preparing the sample for analysis by polarographic technique did not cause the large errors reported by others.

Since chlorine is an oxidant and is known to react with organics, we hypothesized that its addition to seawater could cause changes in the copper-organic complexes we observed in our metal studies. It could reduce the total amount of organics available for complexation with copper or release some of the bound copper.

It was necessary to determine whether the chlorination of seawater would convert complexed copper forms to the toxic or bioavailable ionic form. The electrochemical form of copper was measured with ASV present before

and after chlorination. Seawater samples were spiked with ionic copper, then aged for specific periods of time to allow copper to complex with dissolved organic matter. After aging, the seawater samples contained 5-35 ppb of complexed copper. With the addition of 1.5 ppm chlorine, 1-4 ppb of complexed copper was converted to ionic copper, and the complexation capacity of the water was reduced. In another experiment, however, seawater was spiked with both chlorine and copper, then aged a day. After aging, the copper speciation was similar to unchlorinated seawater, indicating that the chlorination had only a temporary effect on copper speciation. These experiments suggest that chlorination of seawater will increase the amount of bioavailable copper and decrease the complexation capacity of seawater for at least a brief period of time. This fact needs to be integrated in field sampling programs and interpretation of field data relating effluent quantities of metals with bioaccumulation by local species. Further testing is being conducted to define the extent of change caused by different levels and durations of chlorination in seawater.

Ozone Studies

Potentially, ozone could be used in place of, or in combination with, chlorine for treatment of municipal and industrial waste water and to prevent biofouling of power plant cooling systems. To identify the differences of chemical reactions resulting from ozonization of seawater, a series of tests were run, using sodium chloride solutions and natural seawater. The compounds analyzed were: bromine, chlorine, bromate and ozone. All but ozone were identified in chlorinated seawater. The results indicate that ozonization of seawater has chemical results similar to chlorination. Bromide was oxidized to bromine and, eventually, bromate. Ozone also slowly oxidized chloride ions to chlorine, although this reaction is much slower than the bromide to bromine reactions.

When power plant cooling seawater is chlorinated to prevent biofouling, usually enough chlorine is added to produce approximately 1-2 ppm of TRO. Most of this TRO is bromine (assuming low ammonia levels). If ozone was used to produce a TRO level of 1-2 ppm, the major oxidant species would also be bromine. Therefore, the environmental consequences of using ozone in place of chlorine to treat seawater should be similar.

Sediment Studies

Coastal marine sediment is known to be an important reservoir of contaminants such as metals, halogenated organics, and hydrocarbons. Thus, as part of the investigations of the cycling and bioavailability of energy effluent materials, we have conducted field and laboratory studies of the biogeochemical processes occurring in sediment and suspended particulates.

We have emphasized studies on the biogeochemistry of copper, an ecologically important metal that has potential for release, directly or indirectly, by operation of energy technologies. In a laboratory study, ionic copper was added to a sediment/water microcosm previously characterized for physical and chemical variability. Copper was rapidly removed from the water column to the sediment layer. The initial major site of copper sorption was the sediment organic fraction. However, after 4 weeks, a fraction of the copper in the organic material and all of the copper initially sorbed to sediment Fe and Mn oxides was mobilized. Although these studies are ongoing, their preliminary implication indicates that organic material and the oxides of Mn and Fe exert a major control over trace metal partitioning.

Under ambient field conditions in Sequim Bay, sediment organic material and Mn and Fe oxides also appear to be the primary factors controlling metal cycling. In relatively organic-rich sediments, equal amounts of Cu were found to be associated with sediment organic and reductant soluble (Mn-Fe oxides) phases. In sediments containing less organic matter, Cu associated with Mn and Fe oxides predominates. We are preparing a manuscript describing the sediments of Sequim Bay and the relationship of trace metal distribution to sediment parameters.

Organic molecules have a direct effect on metals cycling by providing reactive functional groups that readily coordinate with metals to form stable linkages. They also indirectly affect metal biogeochemistry through changes in pH and Eh caused by microbial metabolic processes. For example, sorption or desorption on hydrous oxides of Mn and Fe occur in response to pH-Eh variations. The chemical and microbiological research are continuing to determine the potential for release of metals from sediments. Separation and analyses of mobile organic compounds produced by sediment microbial processes that influence the bioavailability of metals are a significant part of our study. These studies will be meshed with other investigations by our staff to estimate the accumulative and toxicological effects of organometallic complexes.

The transport of trace metals by suspended particulates was investigated using Sequim Bay as a model tidal system. We found that

the concentration of particulate copper in the surface waters increased significantly during periods of phytoplankton growth. While a normal surface-to-bottom gradient of particulate metals was present, higher surface particulate Cu levels were not due to resuspension of bottom materials since particulate Ti exhibited no seasonal changes. Surface particulate Cu also had areal variations with higher levels occurring at the lower end of the bay. This increase could reflect an accumulation of phytoplankton in that region or the mobilization of sediment-bound Cu in response to reduced oxygen levels. The analysis of additional samples are being completed preparatory to issuing a report describing our observations. Further studies are ongoing to identify the processes controlling the seasonal and areal changes.

Transport of trace metals through the entrance channel of Sequim Bay appears to be related to resuspension of bottom particulates by tidal currents. This observation, based on the comparative distribution of particulate metals, was also noted in surface waters at Admiralty Inlet, which connects Puget Sound to the Strait of Juan de Fuca. Transport of suspended matter through the channel at Sequim Bay in the summer appears to be greater on the flood tide, causing a possible net accumulation of sediment trace metals in the bay. However, limited observations indicate that winter storms may resuspend much of this material for transport on ebb tides.

In addition studies of the transport, cycling and bioavailability of copper were conducted on a series of cruises to Jervis Inlet, B.C., in cooperation with Dr. A. G. Lewis, Institute of Oceanography, University of British Columbia. Preliminary analysis shows that the quantity of suspended matter and concentration of particulate Ti in Jervis Inlet waters is about an order of magnitude less than in Sequim Bay. However, the amount of trace metals in the particulates is such that the concentration of total particulate Cu and Zn is about equal for both waters. The concentration of Mn in Jervis Inlet particulates is about two orders of magnitude greater than in Sequim Bay material, and the increased quantities of particulate trace metals may be due to sorption on Mn oxides.

Model Studies

During FY-77 development began on a hydrodynamic computer model which uses field data to iteratively improve on successive computer model estimates. The purpose of the model is to provide a mass conservative flow field for use on sediment transport, pollutant transport and biotransport models. These transport models require mass conserving flow fields in order to accurately simulate the advection, suspension and deposition of sediments, biota and chemicals in the waterbody. Since advective transport is the dominant mode of transport (as opposed to turbulent mixing) the accuracy of the estimated flow field is paramount to the accuracy of the predicted transport.

Normally, tidal hydrodynamic models solve the full two-dimensional equations of motion to obtain flow field estimates. Obtaining such estimates can often require considerable time, effort, expense and expertise. A rather novel technique has been developed for bypassing some of these problems, provided limited field data are available. By using the stream function equation (with vorticity) one can obtain mass conservative flow fields, provided the vorticity can be estimated. The vorticity is estimated by obtaining the difference between local model computed velocities and field data. The vorticity estimate is now entered into the stream function equation and solved to obtain new velocities. By performing this sequence iteratively, the flow field will be forced closer and closer to the field data and still will be mass conservative. The development of the model is nearly complete and testing will begin early in FY-78.

• Marine Chemistry of Energy-Generated Pollutants

Principal Investigators: E. A. Crecelius, D. E. Robertson, K. H. Abel, D. A. Cochran and W. C. Weimer

This program is designed to increase our understanding of the biogeochemical and physical processes that control the fate of energy-generated pollutants that enter the marine environment. The increased energy needs of our country and increased utilization of the coastlines for siting energy generating facilities and related industries has resulted in the introduction of energy-related pollutants to the oceans from two main sources: 1) the emission of large quantities of material to the atmosphere and subsequent deposition in the oceans, and 2) direct discharges to the oceans from coastal effluents. This program is combined from Chemistry of Ocean Solutions and Geochemical Ocean Sections Study (GEOSECS).

The information generated by this program is vital to the U.S. DOE's interests in understanding: 1) the natural origins, distributions and concentrations in baseline data of trace metals and other contaminants in the oceans; 2) the input rates and mixing rates of pollutants introduced to the oceans; 3) the behavior and fate of the anthropogenic pollutants entering the oceans from the atmosphere and the continents; and 4) an assessment of the potential environmental impact of energy-generated pollutants on the marine environment. Specific tasks that were accomplished during the last year include determining the deposition rate of elements on the Washington Coast, shipboard analysis of mercury in seawater by a new, more sensitive technique, analysis of trace elements in coastal and oceanic waters, and the evaluation of the BLWS for radionuclide sampling.

Atmospheric Deposition of ^{7}Be and Other Elements on the Washington Coast

Atmospheric fallout of anthropogenic dust is a major source of trace metals to coastal marine waters. During the last 2 yr, the concentrations of ^{7}Be and 15 other elements have been measured in air filters and total deposition samples collected at Quilayute on the Washington Coast. These data were used to calculate three parameters: 1) the deposition velocity (Vd), 2) the total elemental deposition/area/yr, and 3) the ratio of element/^{7}Be in air to element/^{7}Be in the deposition collector. With these data, the atmospheric input of elements to coastal waters can be estimated and the atmospheric input to the open ocean can be predicted.

The Vd for elements at Quilayute are shown in Table 7.1. These numbers were calculated by dividing the rate of element fallout (g $m^{-2}yr^{-1}$) by the concentration of element in air (g m^{-3}). The ^{7}Be Vd measured at Quilayute (0.96 cm sec^{-1}) is very similar to that estimated by Young and Siker (1977) off the Washington Coast (1-1.2 cm sec^{-1}). This close agreement between the ^{7}Be Vd strengthens our assumption that Quilayute is a representative site for coastal air chemistry studies. The

TABLE 7.1. Average Annual Deposition Velocity (Vd) for Airborne Elements at Quilayute, Washington, and Ratio of Element/^{7}Be in Air Filters and Deposition Samples

Element	Vd, cm sec^{-1}	Air Element/^{7}Be Deposition/^{7}Be
Cl	6.4	0.11
K	2.6	0.17
Ca	2.6	0.15
Br	2.3	0.30
Fe	0.37	1.30
Mn	0.59	0.60
Ti	0.67	0.50
Cr	0.60	0.50
Pb	0.38	1.50
Se	0.24	1.80
As	0.70	0.30
V	0.24	1.40
Cu	3.00	0.08
Ni	4.00	0.12
Zn	1.80	0.24
^{7}Be	0.96	1.00

Vd for other elements (Table 7.1) can be divided into two groups, those that have Vd of >2 and those <0.7. The high Vd group is believed to be associated with sea-salt aerosols that are typically several μm in diameter. The low Vd group are believed to be of continental origin and in the <1μ size range. The Vd measured at Quilayute are similar to those measured by Cambray in 1975 at six coastal sites on the North Sea. This gives us confidence that our Vd can be applied to all rural coastal and oceanic areas in midnorthern latitudes.

The high Vd for Cu, Ni and Zn have not been explained. These metals appear to be associated with a marine source. A similar effect was reported by Cambray in 1975 for the North Sea.

The ratios of element/^{7}Be in air to element/^{7}Be in total deposition were calculated to determine if ^{7}Be is a good predictor of element deposition in the marine environment. The data in Table 7.1 show that ^{7}Be Vd is a good predictor of elements associated with continental origins (Fe, Mn, Ti, Cr, Pb, Se, As and V), but is a poor predictor of elements associated with marine-derived aerosols (Cl, Br, Ca, K, Cu, Ni and possibly Zn). The conclusion is that ^{7}Be is associated with aerosol of <1μ size and, therefore, has a Vd similar to other elements associated with small aerosol. The elements associated with marine-generated aerosol (sea-salt) has Vd 2-6 times greater than ^{7}Be and, therefore, ^{7}Be deposition rate will greatly underestimate their deposition rates.

The ^{7}Be Vd data for the world oceans and marine air chemistry data will be used to estimate atmospheric input to the ocean of pollutants associated with small aerosols. We plan to compare these atmospheric input rates with other major inputs such as rivers.

Observations of Ultra-low Mercury Concentrations in Oregon-Washington Continental Shelf Waters

Mercury concentrations in ocean water collected off the Oregon-Washington continental shelf have been found to be approximately ten times lower than the best previous measurements. Utilizing a newly developed procedure, which is 50 times more sensitive than previous techniques, measurements of the mercury concentrations in seawater were made on board the R/V Cayuse immediately after the samples were collected. This procedure has greatly reduced the contamination of seawater with mercury during sample storage. Surface seawater was collected in a carefully precleaned plastic pail thrown from the bow of the ship while slowly cruising forward. Deep samples were collected in teflon-coated Niskin Go-Flo® bottles. Immediately after sampling, 800 mℓ of the seawater was transferred to carefully precleaned 1-ℓ Pyrex reagent bottles and acidified with 2.5 mℓ of low-mercury nitric acid and heated in a hot water bath to 60°C. Several minutes after sampling, the mercury was reduced to elemental mercury vapor by adding 20 mℓ of 10% $SnCl_2$ solution and the seawater was purged with nitrogen gas for 12 min at a flow rate of 1 ℓ/min. The purged elemental mercury vapor was collected on a tube of gold-coated glass beads. The gold bead tube was then heated in an induction coil to quickly drive the mercury, in a stream of nitrogen gas, through an LDC® mercury analyzer for detection and quantification. Standard curves were prepared by spiking low-mercury seawater with known quantities of standard mercury solutions and running the spiked samples through the above procedure. The detection sensitivity of this procedure is about 0.1 ng of mercury. Seventeen stations were occupied in Oregon-Washington coastal waters. Samples of Newport Bay and Puget Sound seawater and seawater collected off the Oregon-Washington continental shelf typically contained 0.4 to 1.0 ng mercury/ℓ of unfiltered seawater. These

values are about ten times lower than the best previous measurements which estimated that mercury was present in these waters at a concentration of several ng/ℓ. The ultra-low levels of mercury observed in seawater (0.5 ng/ℓ) are of great significance. They indicate that mercury must have a very short residence time in the oceans. They also mean that phytoplankton, which contains tenths of a ppm of mercury, must concentrate the mercury from seawater by about one millionfold. This efficient bioaccumulation, together with the ultra-low levels of mercury present in the oceans, emphasizes the vulnerability of the marine biosphere to man-made contamination of the oceans by this highly toxic heavy metal.

Trace Element Distributions at Pacific GEOSECS Stations

Instrumental neutron activation analysis of Pacific Ocean GEOSECS seawater samples are establishing the geographical and vertical distributions of Zn, Co, Sb, U, Cs and Rb. In general the concentrations and distributions of these elements are very similar to those observed in the Atlantic Ocean. Extremely low cobalt concentrations averaging around 0.01 µg/ℓ and ranging from 0.006-0.096 µg/ℓ were observed. Considerable variability in the depth distribution of cobalt was observed. Zinc concentrations ranged from 0.56-11.3 µg/ℓ, and averaged about 1.8 µg/ℓ. Zinc concentration maxima existed at discrete depths at each station, but did not systematically correlate with the cobalt maxima. The Sb, U, Cs and Rb distributions were very homogeneous, and averaged about 0.2, 3.5, 0.30 and 120 µg/ℓ, respectively. Preconcentration procedures for measuring arsenic and silver in these samples are presently being conducted.

We have redirected our trace element program towards the continental shelf regions of the Pacific Coast of the U.S. Seawater samples from two cruises in this area are being readied for trace element analysis. We have commenced the analysis of vanadium, an element of considerable interest in the marine environment because of its potential for contamination during oil spills. Vanadium is present in crude oils in relatively high concentrations. The vanadium concentration in Pacific coastal waters off Washington and Oregon is about 1.8 µg/ℓ, and little variability in its distribution in these waters was observed.

Determination of Soluble Aluminum in Seawater

Soluble aluminum levels in seawater are generally thought to be on the order of 1 µg/ℓ; however, few measurements have been made in the past, partially due to limitations in sensitivity and contamination. It is important to assess the levels and variations in soluble aluminum, since one expects particulate aluminum and, thus, possibly soluble aluminum, to vary greatly in coastal environments due to natural processes. It is also possible that anthropogenic activities influence these levels over small areas presently and may be of greater influence in the future.

Toward this end, we have developed a sensitive and quantitative procedure for the determination of soluble aluminum. We utilized an iron hydroxide coprecipitator ion reported previously for determination of arsenic, vanadium, and selenium. Evaluation was conducted using ^{26}Al radiochemical tracer and previously filtered and acidified seawater.

Iron carrier (5 mg) and phenol red indicator were added to six 100 mℓ aliquots of seawater. Sodium hydroxide (1N) was then added dropwise during stirring until the indicator endpoint was reached. The precipitate formed was allowed to age approximately 15 min. It was then centrifuged, the supernatant discarded, and the precipitate then washed with 0.5 M ammonium acetate. The samples were then centrifuged, the supernatant discarded and the final precipitate dissolved in acid and brought to 70 mℓ. The samples and appropriate standards were then γ counted for 1000 min using NaI(Tl) multidimensional gamma ray spectrometers to determine efficiency of recovery during the precipitation procedure. Recovery for the six samples was 99.7 ± 2.0%, indicating the procedure was quantitative and exhibited excellent precision.

Efficiency Evaluation of the Battelle Large Volume Water Sampler

The Battelle Large Volume Water Sampler (BLVWS) has been used for a number of years for concentrating radionuclides from very large volumes of fresh and ocean water (e.g., up to 4000 ℓ). Previous calibrations of this sampler have been conducted during field experiments and in scaled-down laboratory tests. However, no efficiency tests have ever been performed in which large volumes of seawater have been equilibrated with radioactive tracers and then processed through the

BLVWS. This study was conducted to evaluate the adsorption efficiencies for the radionuclides on activated aluminum oxide from large volumes of seawater.

Six 200-ℓ samples of seawater were pumped from Sequim Bay into plastic-lined polyethylene drums and spiked with μCi amounts of the following radionuclides: ^{51}Cr, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{95}Zr-Nb, ^{106}Ru, ^{110m}Ag and ^{144}Ce. The tracers were allowed to equilibrate in the seawater for 2 days and the seawater samples were then pumped through six BLVWS loaded with a series of eight fiberglass filters (30 cm dia) and five beds of 0.7 cm thick by 30 cm dia activated aluminum oxide. The 200 gal spiked seawater samples were diluted with 800 ℓ of raw Sequim Bay seawater before entering the BLVWS by simultaneously pumping from a large reservoir. The combined seawater stream was pumped through the BLVWS at a flow rate of 28 ℓ/min and a total volume of 1000 ℓ of seawater was processed through each sampler. After each sampling, the BLVWS was taken apart and the filters combined for analysis. The five aluminum oxide beds were separately packaged. The filters, oxide beds and plastic drum liners were packaged in standard counting geometries and counted on a large Ge(Li) gamma-ray spectrometer.

During the course of this experiment the amount of tracers lost by adsorption onto the plastic drum liners ranged from 0.05% for ^{124}Sb to 16% for ^{59}Fe. The amounts of particulate species and the percent of the total soluble radioactivity removed on each aluminum oxide bed are shown in Table 7.2.

TABLE 7.2. Efficiency Evaluation of the Battelle Large Volume Water Sampler

	Average % Particulate	Average % of Total Soluble Activity Removed on Each Al_2O_3 Bed				
		1st	2nd	3rd	4th	5th
^{51}Cr	66.2 ± 7.4	55.0 ± 9	14.5 ± 2.1	7.1 ± 1.2	4.3 ± 0.8	2.9 ± 0.4
^{144}Ce	58.0 ± 5.9	96.0 ± 12	11.5 ± 3.6	4.2 ± 1.2	2.5 ± 0.6	2.0 ± 0.5
^{95}Zr	7.4 ± 1.2	73.0 ± 5	16.8 ± 2.9	3.8 ± 1.5	1.1 ± 0.4	0.45 ± 0.13
^{106}Ru	32.7 ± 4.1	49.0 ± 6	18.6 ± 3.2	7.4 ± 1.7	3.8 ± 1.2	2.5 ± 0.5
^{65}Zn	11.1 ± 1.2	85.0 ± 5	8.3 ± 2.2	0.83 ± 0.43	0.30 ± 0.05	0.18 ± 0.03
^{59}Fe	75.9 ± 7.7	59.0 ± 19	23.1 ± 8.3	15.7 ± 4.2	11.6 ± 2.9	8.0 ± 2.3
^{60}Co	5.8 ± 2.3	19.0 ± 3	13.9 ± 2.2	10.0 ± 1.1	7.8 ± 1.0	6.1 ± 0.7
^{54}Mn	20.3 ± 4.3	5.0 ± 1.2	3.5 ± 0.8	2.7 ± 0.5	2.4 ± 0.5	2.0 ± 0.5
^{110m}Ag	26.9 ± 7.7	2.7 ± 1.5	2.3 ± 1.4	1.9 ± 0.9	2.1 ± 1.4	1.9 ± 1.2
^{124}Sb	<1	2.1 ± 0.71	2.4 ± 0.8	2.7 ± 1.0	2.9 ± 1.0	3.2 ± 1.2

Particulate forms (greater than 0.5μ) ranged from <1% for ^{124}Sb to 75.9% for ^{59}Fe. The first Al_2O_3 bed was very efficient in removing ^{144}Ce, ^{65}Zn, ^{95}Zr, ^{59}Fe, ^{51}Cr and ^{106}Ru. The ^{60}Co, ^{54}Mn, ^{110m}Ag and ^{124}Sb retention efficiencies decreased in that order. The first Al_2O_3 bed appeared to be slightly more efficient than succeeding beds, indicating the presence of possibly microparticulates or colloids which might be trapped on the first bed. The retention efficiencies of the second to fifth beds decreased linearly. For the most part the results of this tracer experiment were in good agreement with previous scaled-down efficiency tests.

^{55}Fe and Stable Iron-Comparative Biogeochemical Behavior

Studies of atmospheric aerosols have demonstrated that much of the ^{55}Fe associated with the aerosol input to the oceans is present as either an amorphous or hydrous iron oxide or as very small particulate species attached to the surfaces of the large aerosol particles. By comparison, nearly all of the stable iron is bound in the mineral phase of aerosol particles. This difference in the chemical and physical forms of the radioactive and stable iron isotopes results in the ^{55}Fe being more biologically available than is the stable iron. This difference in availability is responsible for the transfer of a much higher specific activity ^{55}Fe to certain ocean organisms and man than that present in aerosol particles or in seawater. This differential biological uptake of the radioactive iron and its stable element counterpart indicates the problem of always relying on the stable elements in the marine environment to effectively dilute radioelements or other stable elements of anthropogenic sources. The effectiveness of dilution by natural sources depends on the chemical and physical forms of the materials in both the source terms and the receiving environments. The large difference in specific activities of ^{55}Fe in aerosols and seawater relative to ocean organisms reflects the independent behavior of ^{55}Fe and stable iron. Full details of this work are being submitted for publication.

- **In Situ Pollutant Measurements**

Principal Investigator: N. A. Wogman

Other Investigators: K. K. Nielson and H. G. Rieck

This program provides feasibility evaluation, development, and application of instrumental technology for the in situ analysis of the wide spectrum of inorganic, organic, and radionuclide species in ocean and freshwater sediments.

In Situ X-ray Fluorescence System Development

The in situ x-ray fluorescence analyzer developed by this laboratory has successfully measured elemental concentrations in sediment surfaces to water depths of 100 m. With modifications now being incorporated, the equipment will also give accurate measurements down to 6 cm deep in the onsite sediment and allow system use in water depths of 300 m.

Underwater measurements in Puget Sound, Washington were made with in situ x-ray fluorescence equipment mounted in a framework which allowed the probe to just contact the sediment surface. The resulting measurements provided elemental concentrations for the top few millimeters of the sediment column. Although this provided information on current elemental concentrations, greater use could be derived if it were possible to measure elemental concentrations in successive layers of the sediment column. The existing in situ x-ray fluorescence analyzer is currently being modified to provide a system with this capability. Excavating hardware being added can remove a few millimeters of sediment. Following sediment removal the analyzer sensor is lowered to the new surface and the measurement made. This process is repeated successively to a sediment depth of about 6 cm. Excavation of sediment from under the sensor is accomplished by a series of blades attached between roller chains located on each side of the existing x-ray fluorescence analyzer as shown in Figure 7.4.

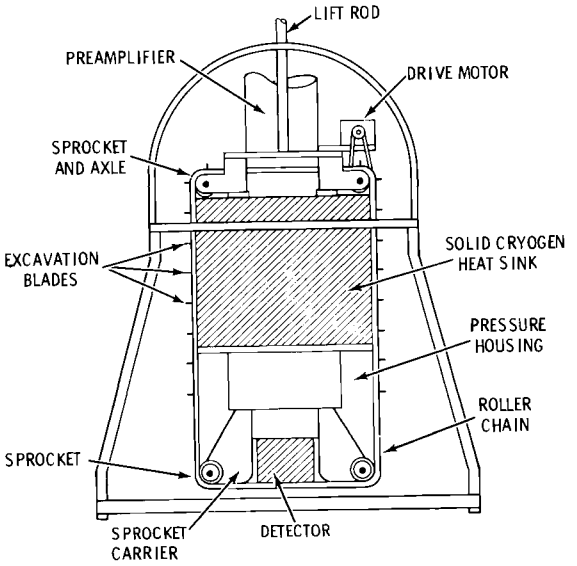

FIGURE 7.4. In Situ X-Ray Fluorescence Probe Modified to Allow Sediment Analysis with Depth.

The pressure housing for the x-ray fluorescence sensor has also been reduced to 7 cm diameter to minimize the excavation area required. The present pressure housing is equipped with a 0.05 mm thick 5-cm diameter Be window allowing operation of the system to water depths of 100 m. By changing to a 0.5 mm thick Ti window, sediments can be analyzed in water depths of 300 m. In the latter

case, ^{241}Am is used to excite the sediment elements instead of ^{109}Cd. The ^{241}Am has a higher energy exciting proton which penetrates the window more easily. The Ti window does decrease the transmission of low energy x-rays (<15 keV), thus, the sensitivity for Fe, Ba, and the intermediate Z elements are reduced by factors of from 3 to 5.

In a typical operation, the modified in situ x-ray fluorescence system will be lowered from a surface vessel or submarine to the sediment region. Following measurement of surface pollutants, power is applied to the excavation assemblies. Chain operation is monitored topside by detection of blade material as it passes under the detector. Shutdown of power releases a brake which allows the x-ray fluorescence system to lower to the new surface and sediment analysis to begin. Use of the modified in situ x-ray fluorescence analyzer is providing knowledge not only of pollutants on the sediment surface but also the changing concentrations of pollutants as a function of sediment depth.

Data Reduction Methods for In Situ X-ray Fluorescence Seabed Analyzer

Continuing method development on data reduction programs allows quantitative analysis of in situ x-ray fluorescence data from the sea bed. Analyses are complicated by the extreme variations in sample matrix (0-90% suspended sediment in water), causing large potential errors from self-absorption, particle size effects, enhancement effects, and the variable mass and volume of sample being "viewed" by the analyzer. A computer code has been developed to relate the backscattered exciting radiation to the mass and average atomic number Z of the material being viewed by the analyzer.

The newly developed computer program estimates appropriate self-absorption, particle size, and enhancement corrections. The measurement of sample mass and average Z is accomplished by separate integration of the coherent and incoherent backscatter peaks and solution of simultaneous equations relating the backscatter intensities to masses of two representative like elements. These representative elements are chosen by the incoherent-to-coherent intensity ratio. Since elements Z greater than 25 are directly measured by fluorescence x-ray peaks, like elements are chosen to represent the Z less than 25 fraction of the sample which comprises most of its mass. Since all mass estimates and corrections are computed from fundamental parameters and an initial spectrometer calibration, the analyses are independent of sample matrix. The light variations in going from fresh water to salt water, or from packed sediments to colloidally-suspended organic matter, are thus accounted for. Preliminary tests with this method suggest a strong correlation ($R^2 = 0.97$) between the computed sample mass and its water content (as determined from grab samples). If further work confirms the relationship, the known water content will permit estimation of the results as part-per-million in sediment, part-per-million in water, or part-per-million in combined suspension.

X-ray Fluorescence Capabilities for Uranium Ore Analysis

A comparison of various instrumental methods has been completed for the determination of uranium in a variety of ores. Included in this comparison were energy dispersive x-ray fluorescence (XRF) methods, wavelength dispersive x-ray fluorescence methods, and several commonly used nonfluorescence photon analysis methods. The XRF methods were examined for both thin and thick samples. Uranium sensitivities and detection limits are compared in Table 7.3. Nearly all of the XRF methods listed provide suitable sensitivity and detection limits for rapid assay of uranium in commercial-grade ores (greater than 0.01% uranium).

Part-per-million uranium detection limits can be routinely achieved using an isotope, secondary source, or direct tube excitation with Si(Li) detectors, or direct tube excitation with wavelength dispersive detectors. The lowest detection limits are obtained with L x-rays for energy dispersive XRF and with either L or M x-rays for wavelength dispersive XRF. Even when uranium standards are not readily available, rapid quantitative analyses may be completed using mathematical methods to compute corrections for an unknown matrix. The XRF capabilities for uranium ore analysis exceed those of direct gamma ray photon spectrometry, or of methods using ^{252}Cf neutron-induced fission activation of the uranium.

TABLE 7.3. Comparison of Bulk Sample XRF Analyses for Uranium.

Peak	Excitation	Detection	Count Rate (c/sec)	Sensitivity (C/S · ppm)	60 sec 3σ Detection Limit (ppm)	Sample
U M_α	Cr Tube, 2.5 kW	Pet		1.1	1.6	71 mg/cm²
U $M_{\alpha\beta}$	^{55}Fe, 35 mCi	Si(Li)	500	0.0093	46.0	63 mg/cm²
U $M_{\alpha,\beta}$	Ti Secondary (1.5 kW W-Tube)	Si(Li)	1000	0.15	20.0	63 mg/cm²
U L_α	Mo Tube, 2.5 kW	LiF (220)		~4.4	2.3	510 mg/cm²
↓	Rh Tube, 12 W	Si(Li)	14,000	0.19	32.0	63 mg/cm²
↓	Rh Tube, 35 W (Pulsed)	↓	20,000	0.38	25.0	63 mg/cm²
↓	Ag Secondary (2.2 kW W-Tube)	↓	2500	0.53	3.6	63 mg/cm²
↓	Mo Secondary (2.2 kW, W-Tube)	↓	2400	1.14	2.8	63 mg/cm²
↓	^{109}Cd, 57 mCi	↓	1400	0.50	3.9	63 mg/cm²
↓	^{109}Cd, 50 mCi	↓	3000	0.56	20.0	In-Situ, Under Water
↓	^{241}Am, 100 mCi	↓	340	0.0057	61.0	63 mg/cm²
↓	^{109}Cd, 3mCi	NaI(Tl), Zr + Y Matched Filters		0.075	~300.0	Field or In-Situ
↓	^{109}Cd, 3mCi	Proportional Counter		0.0033	~400.0	Field or In-Situ
U K_α	^{57}Co 0.5 mCi	Intrinsic Ge	170	0.00071	670.0	1.5 g/cm²